Mineral Resource Report 78

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MINERALOGY ASSOCIATED WITH BURNING ANTHRACITE DEPOSITS OF EASTERN PENNSYLVANIA

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TOPOGRAPHIC AND GEOLOGIC SURVEY
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by **Davis M. Lapham and John H. Barnes**
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U. S. Geological Survey

PENNSYLVANIA GEOLOGICAL SURVEY
FOURTH SERIES
HARRISBURG

1980

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PREFACE

Pennsylvania's anthracite industry has been in decline for many years. One legacy of the former years of more active mining is the large number of waste piles, or culm banks, that were left after many of the deep mines closed. The waste piles can be found throughout the anthracite mining region. They contain a substantial percentage of fine-grained coal and occasionally catch fire, releasing noxious gases to the atmosphere.

A cooperative research investigation was initiated in 1973 to investigate the minerals associated with the burning waste piles. The coal and associated minerals are accumulators of a number of rare elements that are liberated by the fires and transported to the surface of the banks as vapors. The vapors condense on the cool surface of the bank, forming minerals. Through the study of these minerals, one can gain increased understanding of the trace-element fraction in the coal and associated sediments that can be released on combustion. Some of these elements are potentially harmful and some are potentially valuable.

This study should also be of interest to mineralogists. Nineteen minerals never before found in Pennsylvania have been described, including six that are unnamed. One new mineral species has been described as an outgrowth of this research, as has the first known natural terrestrial example of the vapor-liquid-solid growth mechanism. This study has also sparked lively debate among mineralogists as to what constitutes a valid mineral, and it has stimulated research on the environmental aspects and mineralogy of bituminous waste piles in western Pennsylvania.

It is anticipated that this report will be of particular use to mineralogists and many others, including those concerned with the revitalization of the anthracite industry, the gasification of coal as a new source of energy, the restoration of mined land, the maintenance of clean-air standards in the burning of coal, and the utilization of culm or of trace elements that can be derived from coal.

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MINERALOGY ASSOCIATED WITH BURNING ANTHRACITE DEPOSITS OF EASTERN PENNSYLVANIA

by
Davis M. Lapham,[1] John H. Barnes,[2] Wayne F. Downey, Jr.,[3] and Robert B. Finkelman[4]

ABSTRACT

Five burning anthracite waste piles, at Glen Lyon, Shenandoah, Forestville, Williamstown, and Burnside, and one burning anthracite mine, near Glen Lyon, were studied to examine minerals forming as a result of the fires. Minerals identified include selenium, sulfur, galena, pyrrhotite, realgar, herzenbergite, orpiment, bismuthinite, ottemannite, berndtite, hematite, arsenolite, cassiterite, downeyite, salammoniac, cryptohalite, bararite, mascagnite, boussingaultite, potassium alum, tschermigite, gypsum, hexahydrite, epsomite, pickeringite, alunogen, and mullite. Unnamed substances identified were GeS_2, $KAlF_4$, $KAl(SO_4)_2$, $NH_4Al(SO_4)_2$, and $Al_2(SO_4)_3$. Nineteen of these substances had not previously been identified from Pennsylvania. Downeyite is a newly described species (Finkelman and Mrose, 1977, American Mineralogist, v. 62, p. 316-320).

Most of the minerals are believed to have formed by sublimation; several may be alteration products. GeS_2 probably represents the first known natural terrestrial occurrence of the vapor-liquid-solid growth mechanism. Temperature, availability of components, and weather conditions are believed to control distribution. The sources of the components are postulated to be a combination of organically bonded trace elements, minerals in the coal and surrounding sediments, and trash in the waste piles. The presence of an assemblage of tin minerals at Forestville is consistent with a high tin content in the Buck Mountain seam at Zerbe, reported by O'Gorman (1971, unpublished Ph.D. thesis, The Pennsylvania State University).

Steps have been taken by the Pennsylvania Department of Environmental Resources and the U. S. Bureau of Mines to extinguish the fires and restore the land. These efforts should continue, and techniques might be found to extract useful trace elements, perhaps in conjunction with antipollution devices that are needed when coal is burned.

---

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INTRODUCTION

In 1967, the third author, then a high-school student, was searching for plant fossils on an anthracite refuse pile and noticed a cluster of delicate, bright-yellow crystals around a small opening. His curiosity about these crystals (which were arborescent sulfur) has led to research by him, the Pennsylvania Geological Survey, and the U. S. Geological Survey, which has so far resulted in the addition of 14 minerals (plus five presently unnamed compounds) to the list of verified species found in Pennsylvania (Smith and Barnes, 1979). It also has resulted in the naming of a new mineral species (Finkelman and Mrose, 1977) and the description of a growth mechanism never before observed in terrestrial minerals (Finkelman, Larson, and Dwornik, 1974), and has heightened interest in the trace elements and mineral matter present in coal (Finkelman, 1978, 1979; Finkelman, Dulong, and others, 1979; Finkelman, Stanton, and others, 1979). Potential benefits of this study and the derivative studies include the recovery of valuable trace commodities from coal and increased awareness of the environmental hazards posed by burning coal.

This report brings together the data and observations gained from the study of minerals forming as a direct result of the combustion of anthracite refuse piles in eastern Pennsylvania. Fortunately, most of the fires that are described have been extinguished in recent years. However, the information gained in the study of these sites should provide clues to the composition of these and other waste piles still standing, or burning, and the harmful elements that could be released by ignition. It also provides a clue as to what elements could be considered for recovery from the piles. The fourth author has continued research into this subject in the bituminous coal fields from western Pennsylvania to western Virginia. Some of his findings are available as U. S. Geological Survey Open-File Report 78-864 (Finkelman, 1978). His studies have been further extended to trace elements and accessory minerals in unburned coal (Finkelman and Stanton, 1978).

All the localities examined are within the anthracite mining region of eastern Pennsylvania, which extends from Susquehanna County to northern Dauphin County (Figure 1). At one of the localities, the Wanamie mine near Glen Lyon, a coal seam is burning in place. The others are waste piles, although the fire at Kehley's Run mine in Shenandoah has involved both a waste pile and an in-place seam.

The anthracite waste piles, also known as culm banks, boney piles, or gob piles, are composed largely of rock, low-quality coal, and fine-grained residue from the breakers, all of which was removed from the mined coal before shipment to the customer and often was dumped close to the mine. Other residue of the mining operation, e.g., timbers, rails, and equipment, was often conveniently dumped on the piles. Many piles reached heights of 100 m (328 ft) and covered many thousands of square meters (tens of thou-

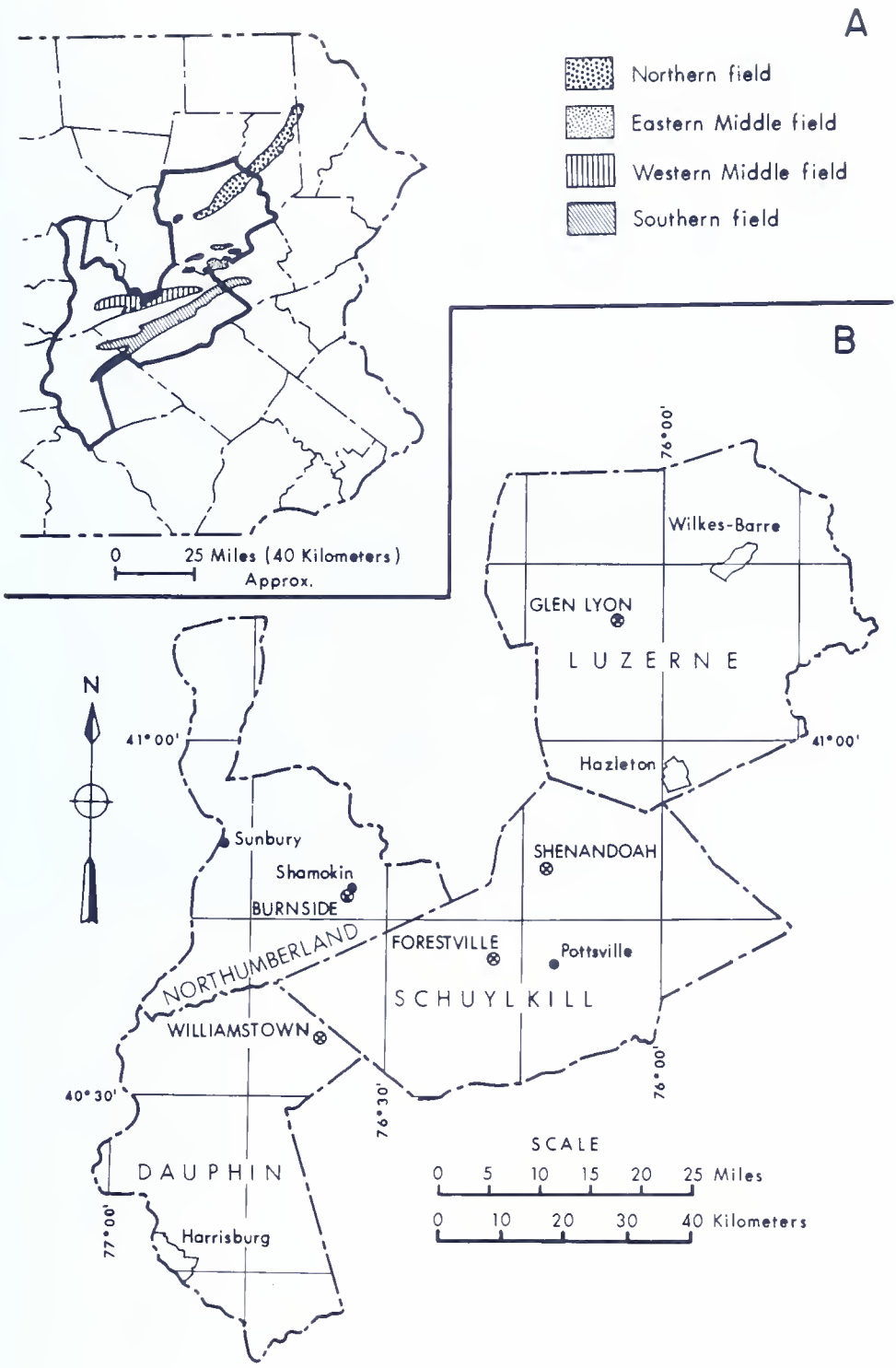

Figure 1. Map of Luzerne, Schuylkill, Dauphin, and Northumberland Counties showing the locations of burning waste piles at Glen Lyon, Shenandoah, Forestville, Williamstown, and Burnside. The burning Wanamie mine is also located at Glen Lyon. Inset shows the four anthracite fields in eastern Pennsylvania.

sands of square feet). Because the living quarters for the miners were also located near the mines, the piles often grew adjacent to populated areas, and there was little regard for the potential hazards they created (Figure 2).

Figure 2. Anthracite waste dumped adjacent to houses, Forestville, Schuylkill County.

As the anthracite industry began to wane in the 1930's, many mining operations were abandoned, and little or no effort was made to remove the waste piles. Eventually, fires erupted in many waste piles; some of them burned for decades. McNay (1971) reported that in 1968 there were 292 burning waste piles in the United States, including 48 in the bituminous fields of western Pennsylvania and 26 in the anthracite fields of eastern Pennsylvania. Many of the fires in Pennsylvania have been extinguished since that time through Operation Scarlift, administered by the Pennsylvania Department of Environmental Resources and the U. S. Bureau of Mines.

Most of the minerals studied were formed by the exhalation of gases produced by subsurface fires. This mode of formation is similar to that of minerals produced by volcanic fumaroles and other geothermal activity. Many of the minerals formed at the burning-anthracite locations have also been

recorded at such localities as Mt. Vesuvius in Italy, The Valley of Ten Thousand Smokes in Alaska, Vulcano in the Eolian Islands, The Geysers in California, and active volcanoes in Central America (Palache and others, 1944, 1951; Lindgren, 1933; Vonsen, 1946; Stoiber and Rose, 1974).

Previous investigations of minerals associated with burning coal include those of Christie (1926), who studied cryptohalite and bararite from the Bararee Colliery in the Jharia coal field, India, and Rost (1935, 1937), who identified the following minerals forming on burning piles of Carboniferous sediments in the Kladno coal district of Czechoslovakia: sulfur, selenium, tschermigite, epsomite, hexahydrite, gypsum, pickeringite, halotrichite, alunogen, copiapite, mascagnite, letovicite, salammoniac, kratochvilite, and other organic substances. Bararite, kratochvilite, and letovicite were first identified and described from these localities. Limacher (1963), in studies of burning waste piles and coal seams in France, identified letovicite, mascagnite, epsomite, hexahydrite, copiapite, melanterite, coquimbite, sodium alum, potassium alum, tschermigite, kaolinite, mendozite, pickeringite, halotrichite, gypsum, sulfur, and salammoniac.

Previous studies of minerals associated with burning coal in Pennsylvania have been somewhat limited. Genth (1875) listed the presence of minute crystals of sulfur together with minute dodecahedral crystals and crystalline crusts of salammoniac at the Burning Mine, Summit Hill, Carbon County. Palache and others (1951, p. 455-456) indicated the presence of small, colorless to yellowish-pink crystals of boussingaultite after a fire in an anthracite-waste pile near Mahanoy City, Schuylkill County. Preliminary abstracts and brief articles related to the present study have been published (Lapham, 1971a, 1971b; Barnes and Lapham, 1971, 1972; Downey, 1974; Finkelman, Lapham, and others, 1974; Lapham, 1975).

The nature of the occurrences and of the minerals presented unusual difficulties to the investigators. Field studies were hampered by the high temperatures near some vents and the emission of noxious gases from the vents, which necessitated short periods of study. Some visitors to the banks complained of headaches and nausea, although the use of gas masks was of some help. One additional hazard is that of subsidence as the fire reduces the coal in the bank to ash. Children playing on a waste pile were killed a number of years ago when the surface collapsed, and the third author nearly plunged into a fiery abyss when the surface collapsed while he was collecting at Kehley's Run mine.

The difficulties posed in the study of the minerals were numerous. One of the principal problems was preserving the material for laboratory study. Many of the minerals form very delicate, arborescent growths in sheltered areas. Sometimes just turning over a rock and exposing these gossamer forms to a gentle breeze causes them to break up and blow away. Extreme care was required in packing such specimens for transport to the laboratory.

A second difficulty is that of hydration of some minerals when they are removed from the hot, dry environment in which they form. For most minerals, the precautions exercised were the use of air-tight containers to house the samples from the time of collection until the time of sample preparation in the laboratory, and promptness in carrying out any planned tests. One mineral, downeyite, proved especially difficult to study because of its extremely hygroscopic nature. The use of a desiccator was required to transport the mineral to the laboratory. Before study could begin, laboratory techniques were devised to prevent the deliquescence of this mineral, which proceeds in a matter of seconds at normal room temperatures and humidities (Finkelman and Mrose, 1977).

Many of the minerals studied consist of extremely small crystals, some of which are less than 100 μm (0.004 in.), thus requiring sophisticated analytical techniques for study and identification. In addition to optical microscopic examination, the following techniques were used for some or all of the minerals:

1. X-ray diffraction to confirm the identity of all the minerals. For some very small samples, electron diffraction was used.
2. Scanning-electron microscopy to observe the surface features of individual grains magnified several thousand times.
3. Transmission-electron microscopy to examine crystal outlines magnified up to 100,000 times.
4. Electron microprobe and energy-dispersive X-ray analyses and wet-chemical analyses to determine composition. Semiquantitative emission-spectrograph analyses were also obtained for several specimens.

ACKNOWLEDGEMENTS

The authors wish to acknowledge assistance from a number of sources in assembling the diverse information contained in this report. Charles Kuebler, John Schimmel, and William Everet of the U. S. Bureau of Mines, Wilkes-Barre, Pennsylvania, provided valuable information regarding the mining history in the vicinity of the fires, the temperature of the fires obtained via borehole measurements, and the local stratigraphy of the anthracite. The staff of the Pennsylvania Department of Environmental Resources, Office of Resources Management, Pottsville District Office, provided information on the efforts of the Commonwealth to reclaim the burned banks through Operation Scarlift. Additional information on the mining history and the history of the fires was provided by George Lebo of the Susquehanna Coal Company, Nanticoke, and by the library staff of the Pottsville *Republican* and the Wilkes-Barre *Record Times-Leader Evening News*. All of the above information was assembled and summarized by Linda Main, a student intern with the Pennsylvania Geological Survey in 1973.

Assistance from the staff of the Pennsylvania Geological Survey has included laboratory assistance by Leslie T. Chubb, who also assisted with specimen and field photography. The supervision of Arthur A. Socolow, State Geologist, and, during the final phases of the project, Bernard J. O'Neill, Jr., Chief, Mineral Resources Division, is appreciated.

The authors also wish to thank Robert C. Smith, II, of the Pennsylvania Geological Survey, and Michael Fleischer and Peter Zubovic of the U. S. Geological Survey, Reston, Virginia, for their thoughtful and helpful criticisms of the manuscript. The help of Mary Mrose of the U. S. Geological Survey and other staff members of the U. S. Geological Survey and the Pennsylvania Geological Survey is also gratefully acknowledged.

It should also be noted that this study was begun in 1973 under the leadership of the late Davis M. Lapham. It was Dr. Lapham who set the outline and style for this report, and some sections remain exclusively of his authorship. All sections of this report were extensively reviewed by him, and the other authors have attempted to carry out his wishes to the best degree possible.

GEOLOGIC SETTING

The anthracite and associated sedimentary rocks of eastern Pennsylvania are preserved in structural depressions in the eastern part of the Appalachian Mountain section of the Valley and Ridge physiographic province. They are bounded by older rocks of the Pennsylvania culmination of the Valley and Ridge province on the west, the Allegheny and Pocono Plateaus on the north and east, and the Great Valley on the south. The Anthracite region is divided into four fields: the Northern field, the Eastern Middle field, the Western Middle field, and the Southern field (Figure 1).

In general, the intensity and complexity of both folding and faulting increase southward; that is, fold asymmetry, fold overturning, narrow fold hinges, reverse faults, and tear faults become more prevalent toward the south (Wood and Bergin, 1970). In part, however, this complexity is distributed vertically and is related to differing relative rock competence under regional and local stresses (Wood and others, 1969; Wood and Bergin, 1970). Major structural elements of the Appalachian Mountain section carry eastward into the region and die out against the Pocono Plateau. These major anticlinoria and synclinoria control the extent and location of the four anthracite fields (Figure 3), the deepest being the Southern field in the Minersville synclinorium. It has been proposed that high-angle reverse faults throughout the region were generated by major thrust faults within less competent units at depth (see summaries by Wood and others, 1969, and Wood and Bergin, 1970).

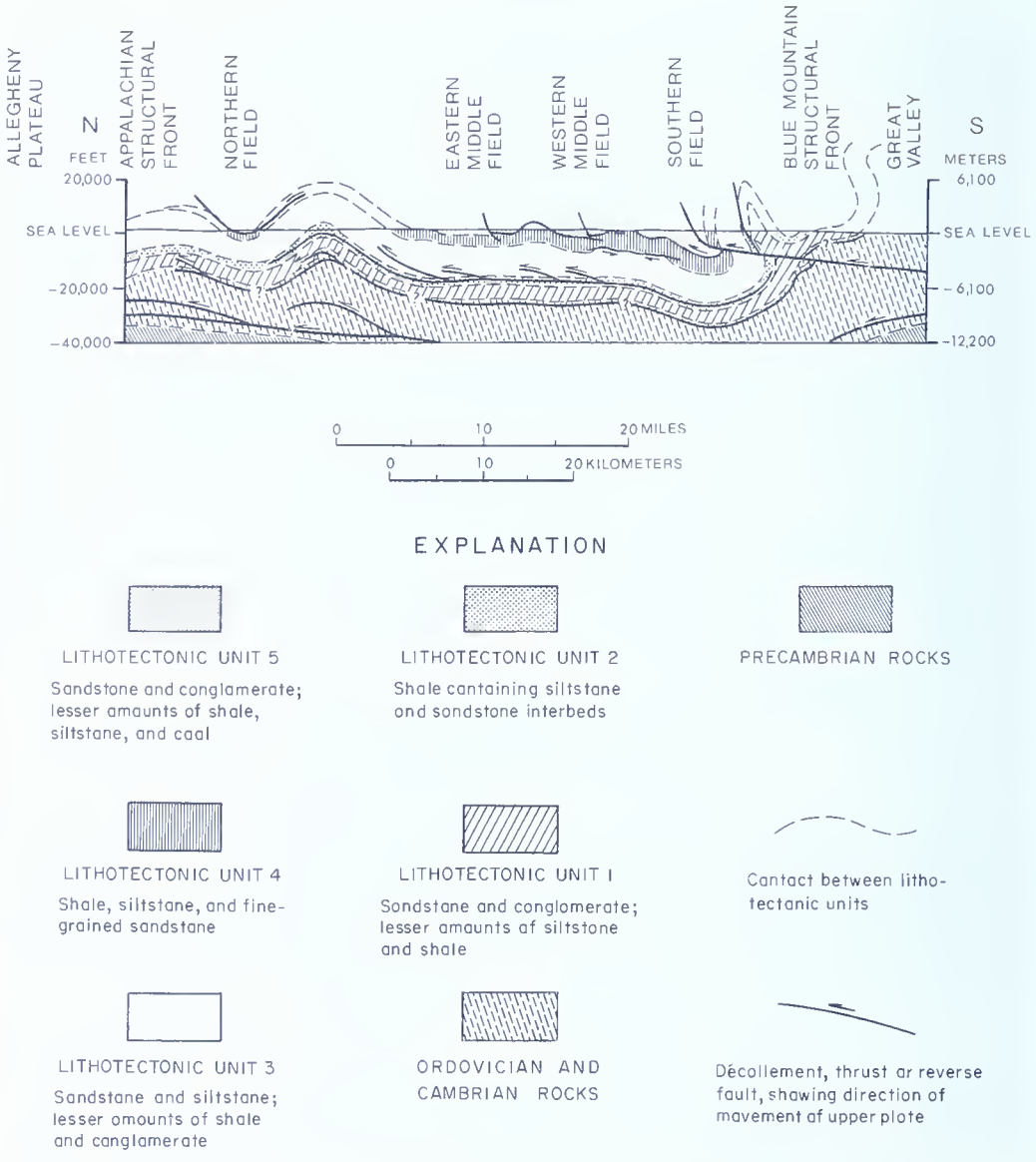

Figure 3. Cross section of the Anthracite region of eastern Pennsylvania (after Wood and Bergin, 1970, Figure 3).

The major stratigraphic units in the Anthracite region are, from oldest to youngest, the Catskill Formation of Late Devonian age, the Spechty Kopf Formation[1] of Late Devonian and Early Mississippian age, the Mississippian Pocono and Mauch Chunk Formations, and the Pennsylvanian Pottsville and Llewellyn Formations (Berg and others, 1980, in preparation). The Upper Devonian section is composed largely of red sandstone and shale, the Mississippian of gray conglomerate and red siltstone, shale, and sandstone

[1] According to U. S. Geological Survey usage, the Spechty Kopf is a member of the Catskill Formation.

(although the Pocono is a rather white sandstone). The Pennsylvanian section consists of gray conglomerate, sandstone, siltstone, and shale, and has red units at the base and numerous interspersed anthracite beds. Evidence suggests that the lower part of the Llewellyn Formation is equivalent to the Kittanning Formation, a major bituminous-coal-bearing unit of western Pennsylvania (Wood and others, 1969; Darton, 1940).

The relation of the anthracite of the eastern part of the state to the bituminous coal of the western part of the state has been the subject of considerable discussion and has been summarized by Wood and others (1969). The change from low-rank coal in the west to high-rank coal in the east has been ascribed to a greater depth of burial eastward, to differences in composition, and to increasing deformation eastward. Recent work has shown that fixed-carbon content parallels major fold structures and, therefore, that, in addition to depth of burial, deformation might have been a major factor in controlling coal rank (Wood and others, 1969). Eastern Pennsylvania underwent several episodes of deformation throughout the Paleozoic Era, culminating in the Appalachian orogeny at the end of the Paleozoic.

Topographically, the Anthracite region consists largely of parallel, linear ridges and valleys that trend approximately N60E. In the areas studied, relief ranges from about 150 m (about 500 ft) to about 300 m (about 1000 ft) near Williamstown. The topography is an expression of differential erosion of units exposed by the various folds. The Pottsville and Pocono sandstones are more resistant units and, where exposed, are typically ridge formers (Thornbury, 1965, p. 113). The region typically exhibits a trellis drainage pattern characterized by numerous water gaps. Major drainage is through the Susquehanna, Schuylkill, and Lehigh Rivers.

LOCALITIES

Five localities were studied in detail: two in the Northern field, one in the Western Middle field, and two in the Southern field.

The locations in the Northern field are near the borough of Glen Lyon (Figure 4). One is a waste pile approximately 0.5 km (0.3 mi) north of the community at 41°10′40″N/76°04′40″W in Newport Township, Luzerne County. The pile (Figure 5) is estimated to be 460 m (1,500 ft) long by 150 m (500 ft) wide, and to have a maximum thickness of about 40 m (130 ft) (Stingelin and Knuth, 1970). As is true of all waste piles, the origin of the contents is uncertain. The Pottsville and Llewellyn Formations are both present in this area. The Llewellyn, which contains 17 coal seams, the thickest of which is 4 m (13 ft), is the major producer (Hollowell and Koester, 1975). Darton (1940) reported that coal mining at Glen Lyon probably extended to a depth of about 200 m (650 ft). The following coal seams were

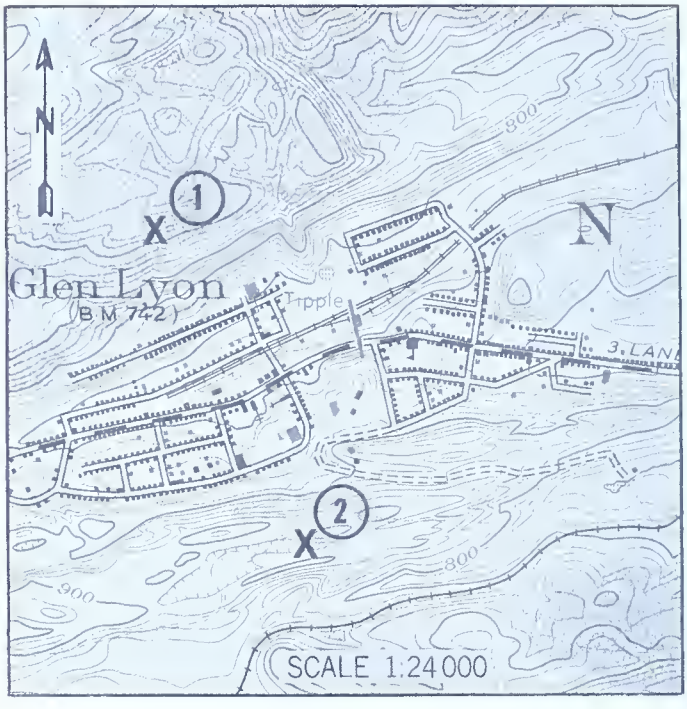

Figure 4. Locations of (1) Glen Lyon waste pile and (2) Wanamie mine, Luzerne County, shown on part of the Nanticoke 7½-minute quadrangle (U. S. Geological Survey, 1954).

Figure 5. Burned waste material (light-colored area) at the top of a mountain north of Glen Lyon.

listed by Darton as being present in this area (top to bottom): Abbott, Kidney, Hillman, Top Baltimore (Cooper), and Baltimore. To add to the uncertainty, it has been reported that waste is sometimes shipped a distance of 20 km (12 mi) or more from mine to waste pile (W. Everet, personal communication, 1973). In addition, there is no way to determine what other debris could have been disposed of at this location.

The fire is believed to have started in 1932 on a nearby bank and to have spread to the main bank in the 1950's (George Lebo, personal communication, 1973). In 1971, airborne studies indicated that 29 percent of the area of the bank was included in the fire. Boreholes drilled into the bank indicated a temperature of 730°C (1346°F) at a depth of 11 m (36 ft). Airborne measurements in May 1971 indicated a surface temperature as high as 25°C (77°F) and a background temperature of 15.5°C (60°F) (Stingelin and others, 1971, p. 44-45). Temperatures of individual vents were measured in 1971-1972 at 100°C (212°F) to 300°C (572°F).

The second location in the Northern field is the Wanamie mine, the only in situ coal seam studied (Figure 6). This mine is 0.6 km (0.4 mi) south of Glen Lyon and 3.2 km (2.0 mi) west of Wanamie, at 41°10′10″N/76°04′25″W in Newport Township, Luzerne County (Figure 4, site 2). Two coal seams are believed to be included in the fire, the Hillman and the Diamond or Lower Stanton ("Baltimore") seams of the Llewellyn Formation (W. Everet, personal communication, 1973).

The fire started in 1956 following a mine train accident. Airborne measurements in April 1972 indicated that the fire encompassed an area of 8,000 m^2 (86,000 ft^2) and produced surface temperatures of 40.5°C (105°F) with a background temperature of 24°C (75°F) (Knuth and Stamm, 1972). Measurements at individual vents in 1971-1973 indicated minimum temperatures of 80°C (176°F) to 345°C (653°F).

The fire in the Western Middle field is at Kehley's Run mine in West Mahanoy Township, on the northern boundary of Shenandoah, Schuylkill County, at 40°49′30″N/76°12′00″W (Figure 7). Most samples studied were collected from the burning waste pile, although this fire has also included in situ coal (Figure 8). Three coal seams are believed included in the fire, the south-dipping Mammoth, Skidmore, and Seven Foot coals of the Llewellyn Formation. Refuse from these and other seams in the area, including the Buck Mountain coal of the Sharp Mountain Member of the Pottsville Formation, could have been present in the waste pile (Wood and Arndt, 1969). The nature and quantity of foreign matter in the waste pile cannot be determined. Several thrust faults present in this area are parallel to strike (N70–75E) and dip southeast. The Kehley Run fault is approximately 0.2 km (approximately 660 ft) east of the mine. The Park Place fault is assumed to end before reaching the mine, approximately 0.8 km (0.5 mi) to the northeast (Wood and Arndt, 1969).

Figure 6. Smoke billowing from the ground above a burning coal seam at the Wanamie mine.

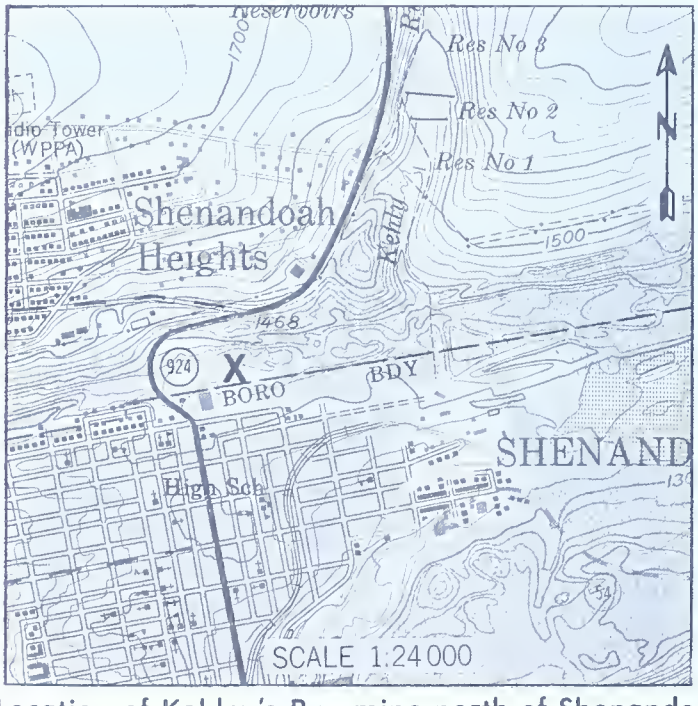

Figure 7. Location of Kehley's Run mine north of Shenandoah, Schuylkill County, shown on part of the Shenandoah 7½-minute quadrangle (U. S. Geological Survey, 1955).

Figure 8. A portion of the excavation of Kehley's Run mine made in an attempt to extinguish burning coal seams (May 1974).

This fire is the second recorded at Kehley's Run mine. The first, in 1880, took five lives and was extinguished in 1881 by sealing the mine openings with clay and flooding the mine (O'Brien, 1965). The second fire started in 1957. Early attempts to extinguish it failed. By 1971, an area of about 56,000 m^2 (603,000 ft^2) was burning. Airborne-infrared studies indicated a surface temperature of 30°C (86°F) and a background temperature of 17°C (63°F) (Knuth and Stamm, 1972). Minimal temperatures of individual vents in the culm, recorded in 1970 and 1971, ranged from 100°C (212°F) to 300°C (572°F).

The Forestville waste pile is one of two studied in the Southern field. This bank is 0.3 km (0.2 mi) north of the community of Forestville at 40°41′42″N/76°17′50″W in Cass Township, Schuylkill County (Figures 9 and 10). This area contains many thrust and high-angle reverse faults parallel to strike (approximately N75E) that are believed to branch from the Pottchunk and Mauchono décollements (G. H. Wood and M. D. Carter, unpublished tectonic map of Anthracite region of Pennsylvania).

Table 1 lists the coal seams that have been mined in the west-central part of the Southern field. Of these, the coal seams in the Tumbling Run Member of the Pottsville Formation are probably least important at Forestville. Those of the Schuylkill Member are more likely present, and those of the

Figure 9. Location of the Forestville burning waste pile, Schuylkill County, shown on part of the Minersville 7½-minute quadrangle (U. S. Geological Survey, 1955).

Figure 10. Burned waste material (light-colored areas) at Forestville, Schuylkill County.

Table 1. *Coal Seams Mined in the West-Central Part of the Southern Anthracite Field (after Wood and others, 1969)*

System	Series	Formation	Member	Coal	Comments
PENNSYLVANIAN	Upper and Middle Pennsylvanian	Llewellyn		Tracy No. 16	Mined(?) (= Cockle coal bed).
				Diamond No. 14	At Forestville, mined intensively.
				Primrose No. 11	Mined(?).
				Holmes No. 10	Youngest at Williamstown.
				Top Split Mammoth No. 9	(= White Ash or Four Foot coal bed).
				Middle Split Mammoth No. 8-1/2	(= Seven Foot or Middle Branch coal bed).
				Bottom Split Mammoth No. 8	Maximum thickness at Forestville (= Black Heath coal bed).
				Skidmore No. 7	Probably mined at Forestville; mined as Top Split coal bed at Williamstown.
				Seven Foot No. 6	Mined(?).
				Buck Mountain No. 5	(= Skidmore No. 7 at Williamstown).
	Middle Pennsylvanian	Pottsville	Sharp Mountain	Little Buck Mountain No. 4	Crops out in Forestville syncline and mined nearby; absent at Williamstown.
				Scotty Steel No. 3	Mined(?).
	Lower Pennsylvanian		Schuylkill	Lykens Valley No. 2	Probably mined at Williamstown; too thin at Forestville(?).
			Tumbling Run	Lykens Valley No. 4	Absent at Forestville.
				Lykens Valley No. 5	Important at Williamstown; some at Forestville.
				Lykens Valley No. 6	May be mined at Forestville and Williamstown.

Sharp Mountain Member of the Pottsville are certainly present. The Little Buck Mountain No. 4 coal is restricted to this area. The larger producer is the Llewellyn Formation, which is thicker here than elsewhere, attaining a maximum of 1,000 m (3,280 ft) (Wood and others, 1969). There are about 40 coal beds within the Llewellyn Formation in this area (Wood and others, 1969). The Llewellyn also contains more metamorphic rock fragments here, suggesting greater proximity to a source area, and more heavy-mineral detritus in the coal.

The fire at Forestville was discovered between 1945 and 1955. The bank covers 89,000 m^2 (958,000 ft^2). It was estimated that 26.5 percent of that area was involved in the fire in 1971 (Knuth, 1971). Surface temperatures of 30°C (86°F) were recorded, and temperatures of individual vents in 1972-1973 ranged to a maximum in excess of 660°C (1220°F).

The other fire in the Southern field was at a culm bank 1 km (0.6 mi) north of Williamstown at 40°35′25″N/76°36′50″W in Williams Township, Dauphin County (Figures 11 and 12). High-angle reverse faults are common parallel to strike (approximately N75E). One, the South Branch Big Lick Mountain fault, passes through the mine from which the Williamstown culm probably was derived. This area is apparently not as intensely faulted as the Shenandoah or Forestville area (Wood and Trexler, 1968).

The coal horizons at Williamstown are nearly the same as those at Forestville (Table 1), although stratigraphically lower coals would be more im-

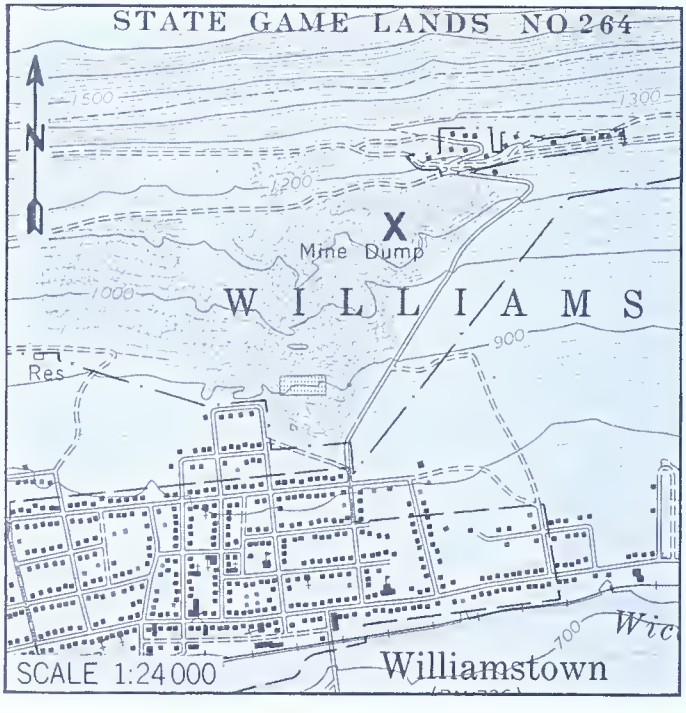

Figure 11. Location of the Williamstown waste pile, Dauphin County, shown on part of the Tower City 7½-minute quadrangle (U. S. Geological Survey, 1969).

Figure 12. General view of the Williamstown burning waste pile, Dauphin County.

portant at Williamstown. Probably the greatest difference between these localities is a thickening of the Pottsville Formation in the direction of Williamstown. The three uppermost Llewellyn coals at Forestville are absent at Williamstown (Wood and Trexler, 1968; Wood and others, 1969).

The fire at Williamstown is believed to have started about 1930, or earlier. An airborne-infrared study in 1971 indicated that of a total area of approximately 127,000 m^2 (1,367,000 ft^2), 21 percent was burning. This study also indicated a maximum surface temperature of 26 °C (79 °F) and a background temperature of 13 °C (55 °F). Boreholes drilled in the same year encountered a maximum temperature of 376 °C (709 °F) at a depth of 8.5 m (28 ft) (Stingelin and others, 1971, p. 64-65). Measurements at individual vents in 1971-1972 indicated a maximum temperature of 200 °C (392 °F).

Some samples were obtained from a sixth locality, which was studied in less detail than the others. This locality is a burning waste pile at Burnside, Northumberland County, in the Western Middle field. It is approximately 1.5 km (0.9 mi) south-southwest of Shamokin, at 40°46′14″N/76°34′12″W (Figure 13).

The causes of the fires at these localities are open to some speculation. The only fire for which the origin is known is that at the Wanamie mine. In 1956, a mine train was involved in an accident, knocking down electrical wires. Because it was carrying dynamite, initial efforts were directed toward the successful removal of the train and its contents. The fire quickly spread

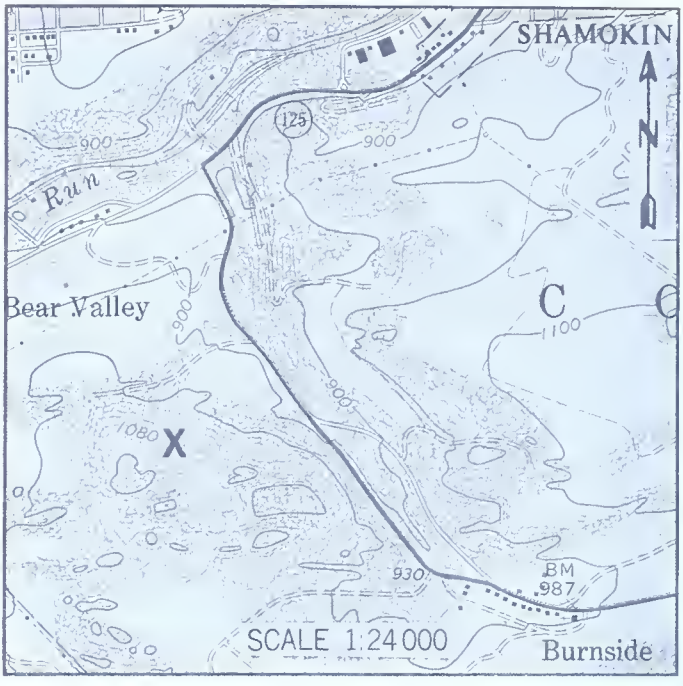

Figure 13. Location of the Burnside burning waste pile, Northumberland County, shown on part of the Shamokin 7½-minute quadrangle (U. S. Geological Survey, 1969).

through timbers to the coal (W. Everet, personal communication, 1973). At Kehley's Run mine, it is known that in 1957 an engine house caught fire and embers fell into the mine opening, igniting coal and timbers (T. P. Flynn, Jr., personal communication, 1973). The cause of the fire in the engine house is unknown, the two most likely causes being children playing with matches or an act of revenge by miners caught bootlegging coal from the mine.

Very little is known about the causes of the fires at the other locations. The most probable causes are spontaneous combustion, careless burning of trash, and intentional ignition to obtain "red dog," the brick-red residue of these fires that is useful as a paving material. Limacher (1963) concluded that similar fires that he studied in France probably started by spontaneous combustion. Factors that he believed would favor the likelihood of spontaneous combustion include a low degree of metamorphism; the presence of enough joints to permit circulation of oxygen, but not enough to cool the coal excessively; the presence of molds that can grow on wood, rags, and other organic material in the waste pile and elevate the temperature to as much as 150°C (302°F), speeding the oxidation of sulfides; and the presence of significant amounts of sulfide minerals, organic sulfur, and humic materials in the coal (Limacher, 1963, p. 287). Research by Jones and Scott (1939) is in agreement with Limacher's conclusion that the rank of coal affects probability of spontaneous combustion. Their evidence indicates that

most anthracite has an ignition temperature too high to be reached by normal oxidation processes that could lead to spontaneous combustion. They believe that other substances in the bank, such as oil-soaked lumber and rags, hay, and manure could cause fires to begin by spontaneous combustion. The oxidation of sulfides in a waste pile that has restricted air circulation might alone produce sufficient heat to cause combustion. The United Verde mine fire at Jerome, Arizona, consists of a burning sulfide ore body, which is believed to have ignited by the spontaneous combustion of unstable sulfide minerals when they were exposed to air (Anthony and others, 1977, p. 29).

MINERALOGY

INTRODUCTION

For all of the substances subsequently described, a question can legitimately be asked as to whether they are minerals. The question arises for these substances because their origin ultimately is man-dependent; that is, the coal of the area was mined by man and the fires at these mine sites may have been either directly or indirectly caused by man. Most definitions of a mineral include a phrase such as "natural occurrence" and suggest more or less explicitly that man and his activities are not included in the scheme of mineralogy or in the realm of nature. After much consideration, our belief is that all the substances from areas of burning anthracite described herein should be classified as minerals, that an arbitrary distinction between man and nature is neither possible nor advantageous, and that the problem largely is one of semantics and usually will disappear upon a discussion of the origin of the material in question (Lapham, 1973, from a paper presented to Pennsylvania Minerals Symposium, Friends of Mineralogy, Region 3).

In a simplistic world where man is only an observer and recorder, there is little problem because, by all definitions, a natural occurrence becomes synonymous with everything that man finds. However, it is man's nature to modify his environment in ways that either directly or indirectly result in the formation of substances that otherwise would not have existed. For example, stalactites grow upon the cement of road overpasses, secondary sulfates crystallize on the walls of underground mines, fission products are created by nuclear reactions, and gems are synthesized in laboratories. Although an arbitrary distinction may be made between purposeful and accidental formation, such a distinction may be difficult (as in nuclear experimentation, where fission products are known and necessary by-products but are not the primary objective) or not particularly meaningful when a clear and accurate origin is presented. In some cases, the extent of the role of man may not be clear, as in substances that result from a forest fire, the cause of which can range from lightning to arson, or, indeed, substances

that result from burning anthracite where the origin of the fire is equally uncertain. For such substances, an arbitrary distinction based upon the interference of man, purposeful or accidental, is impossible.

With regard to the "naturally occurring" clause of most mineral definitions, the authors submit that if an inorganic substance can theoretically occur, by means that are not man-induced, in terrestrial or known extraterrestrial environments, it certainly deserves mineral nomenclature. The substances discussed here have formed by processes common to fumarolic or volcanic environments; many have been described from occurrences where man clearly has not intervened (see, for example, Stoiber and Rose, 1974). They are not purposeful products, and the role of man in their crystallization is both remote and uncertain. For these reasons, the authors refer to them as minerals and think that all of them should be considered as such.

Table 2 is a list of all of the verified minerals described herein that are believed to have formed as a direct or indirect result of the anthracite fires, and the locations at which the minerals were found. This list is by no means complete, as the occurrences are so heterogeneous, and the minerals, in some cases, are present in such small, intimately mixed assemblages, that a complete, comprehensive mineralogy could not be determined. The order of listing of minerals in Table 2, and the order of the following presentation, is according to the Dana system (Palache and others, 1944, 1951).

NATIVE ELEMENTS

Selenium

Formula: Se

System: Hexagonal

Habit: Most commonly as black, metallic, hexagonal prisms, sometimes hollow (Figures 14 and 15). Also as red, vitreous, transparent material that is amorphous to X-rays, and as gray, amorphous, metallic spherules. Prisms, up to 20 mm (0.8 in.) in length, often branching and twinned. Twins meet at 30- and 60-degree angles. Etch lines or growth lines common on prism faces. Crystals are soft (hardness = 2) and ductile.

Occurrence: Ten- to 20-mm (0.4- to 0.8-in.) crystals were common at Glen Lyon and Forestville, usually in voids and in vent openings. One- to 5-mm (0.04- to 0.2-in.) crystals were found over large areas on and below the surface at Williamstown, and in limited areas at the Wanamie mine. Amorphous selenium was found at Glen Lyon.

Associations: Vents containing selenium are commonly surrounded by sulfur, and in many places, an intermediate zone of dark-red crystals, possibly "selen-sulfur," is present. Downeyite crystals were observed on selenium at Glen Lyon. Some selenium had droplets of a clear, colorless liquid, possibly the residue of downeyite. Amorphous metallic spherules of selenium were associated with cryptohalite (Figure 16).

Table 2. *Minerals Identified in Association with Burning Anthracite in this Study**

Mineral	Formula	Abundance					
		Glen Lyon	Wanamie	Shenandoah	Forestville	Williamstown	Burnside
NATIVE ELEMENTS							
Selenium†	Se	Common	Minor		Common	Minor	
Sulfur	S	Common	Minor	Common	Common	Common	
SULFIDES AND SELENIDES							
Galena	PbS			Minor			Minor
Pyrrhotite	$Fe_{1-x}S$						Minor
Realgar†	AsS	Rare					
Herzenbergite†	SnS				Trace		
Orpiment†	As_2S_3						Rare
(unnamed)†	As_2Se_3						Rare
Bismuthinite	Bi_2S_3				Trace		
Ottemannite†	Sn_2S_3				Trace		
Berndtite†	SnS_2				Rare		
(unnamed)†	GeS_2				Rare		
OXIDES							
Hematite	Fe_2O_3	Common	Common	Common	Common	Common	
Arsenolite†	As_2O_3						Rare
Cassiterite	SnO_2				Rare		Rare
Downeyite†	SeO_2	Rare			Rare	Rare	Rare
HALIDES							
Salammoniac	NH_4Cl			Common			
(unnamed)†	$KAlF_4$				Trace		
Cryptohalite†	$(NH_4)_2SiF_6$	Common		Common			
Bararite†	$(NH_4)_2SiF_6$			Rare			

Table 2. *(Continued)*

Mineral	Formula	Abundance					
		Glen Lyon	Wanamie	Shenandoah	Forestville	Williamstown	Burnside
SULFATES							
Mascagnite†	$(NH_4)_2SO_4$	Rare		Rare		Rare	
(unnamed)†	$KAl(SO_4)_2$				Trace		
(unnamed)†	$NH_4Al(SO_4)_2$		Common			Common	
(unnamed)†	$Al_2(SO_4)_3$	Minor	Minor			Common	
Boussingaultite	$(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$	Rare					
Potassium alum	$KAl(SO_4)_2 \cdot 12H_2O$	Rare					
Tschermigite	$NH_4Al(SO_4)_2 \cdot 12H_2O$	Common	Common			Common	
Gypsum	$CaSO_4 \cdot 2H_2O$		Rare		Minor		
Hexahydrite	$MgSO_4 \cdot 6H_2O$		Minor				
Epsomite	$MgSO_4 \cdot 7H_2O$		Minor				
Pickeringite	$MgAl_2(SO_4)_4 \cdot 22H_2O$				Rare		
Alunogen	$Al_2(SO_4)_3 \cdot nH_2O$ n = 16, 17, or 18	Common	Common			Common	
SILICATES							
Mullite†	$Al_6Si_2O_{13}$					Rare	

*Because of the nature of the occurrences, the mineralogy of each occurrence cannot be considered to be complete. Only minerals verified by X-ray diffraction or other means are listed. Additionally, other minerals not directly related to the fires were observed, e.g., quartz, goethite, muscovite, kaolinite, and other clay minerals.

†First verification of this mineral in Pennsylvania (Smith, 1978; Reed, 1975; Montgomery, 1969; Gordon, 1922; Genth, 1875; Rogers, 1858).

N.B.: An additional fire-related mineral, letovicite [$(NH_4)_3H(SO_4)_2$], was collected from a waste pile near Laurel Run, Luzerne County, in August 1979 by Wayne Downey, and verified by X-ray diffraction by Robert Finkelman. This is the first verification of letovicite in Pennsylvania.

Figure 14. Cluster of hollow, hexagonal selenium crystals from Glen Lyon. The longest crystals are from 1 to 2 cm (0.4 to 0.8 in.) in length.

Origin: Sublimation. The spherules might be a condensate. The red vitreous material appears to have been melted and resolidified (melting point = 217°C, or 422.6°F).

Identification: X-ray diffraction and energy-dispersive X-ray analysis of hexagonal crystals, color, crystal morphology, hardness. Emission-spectrographic analysis of a hexagonal crystal from Glen Lyon indicated the presence of minor Al and trace Ge, Cu, Mg, Mn, Si, and Fe.

Sulfur

Formula: S

System: Orthorhombic

Habit: Variable, but rounded forms (Figure 17) and orthorhombic faces having simple crystallographic indices (Figure 18) are most common. Rounded forms in particular may be combinations of higher order indices. Most single crystals are very thin, flat plates having a large 001 face (Figure 19) or rather thin dipyramids (Figure 20), both orthorhombic. Other single crystal forms are rare, especially elongate laths believed to be monoclinic (Figure 21). Long spears of sulfur that lack recognizable faces are common and could be either orthorhombic or monoclinic. Some forms have not been noted previously in the literature (Figure 22); others

Figure 15. Scanning-electron photomicrograph of a hollow selenium crystal from the Glen Lyon waste pile. 474X. Courtesy of Dr. A. J. Thomas, Director, Biodynamics Research Laboratory, Rockville, Maryland.

Figure 16. Sketches of amorphous spherules of selenium on columns of cryptohalite.

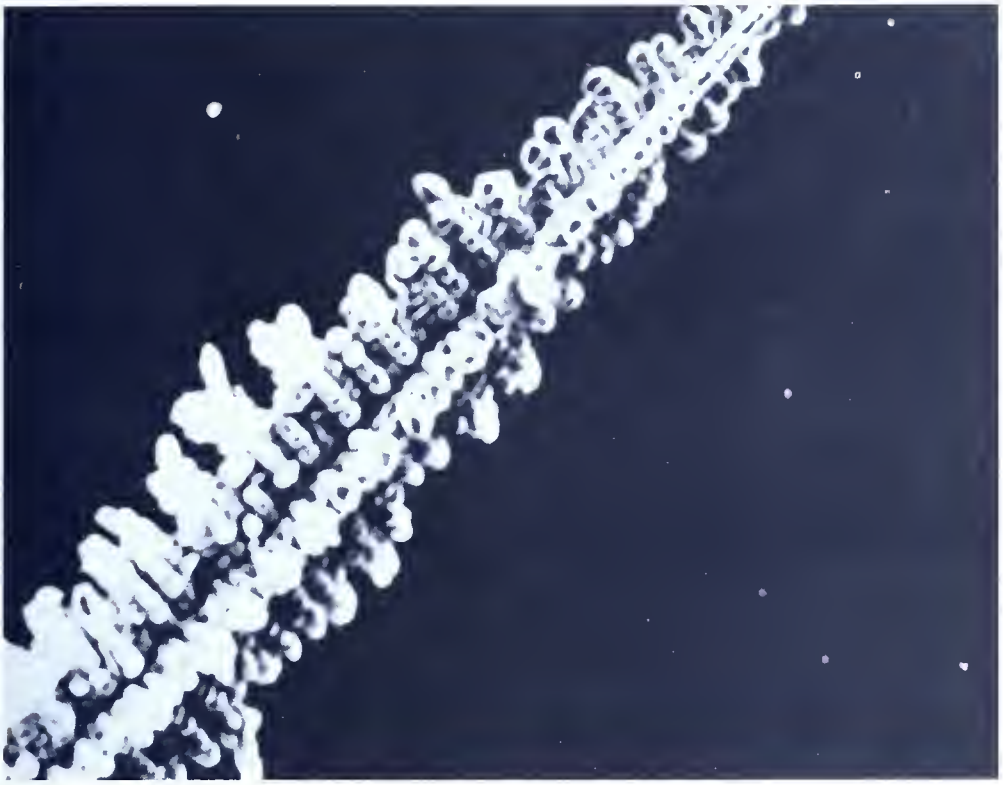

Figure 17. Scanning-electron photomicrograph of a spire composed of rounded forms of orthorhombic sulfur from Glen Lyon.

are similar to synthetic forms or theoretical conceptions (Figure 23) as noted by Goldschmidt (1922, Tafeln, v. 8, Tafel 22). Rarely, forms believed to be cyclic twins have been observed (Figure 24), but none exhibited the typical reentrant angles of twins. Crystal groups of penetration twins and amorphous forms (Figure 25) are abundant; the latter are more closely associated with selenium and probably are intermixed with it. Minute orange-red sulfur balls are intermixed with crystalline sulfur, but are most abundant at the perimeter of crystal aggregates. Skeletal to dendritic or flowerlike aggregates of sulfur are common, but crystal faces rarely can be identified (Figure 26). Neither interfacial angles nor axial lengths were measured; thus, the axial orientations and face indices are based on analogies with published data (Goldschmidt, 1922; Palache and others, 1944). The color of most sulfur when collected was bright yellow to dark greenish yellow. After several months of storage, the color faded to a lighter yellow. Near selenium growths, the sulfur grades from yellow through orange to deep red over a distance of 1 to 2 cm (0.4 to 0.8 in.) toward the selenium.

Occurrence: Minute crystals coated the ground on all the waste piles. Larger crystals were concentrated in roughly circular areas, from several

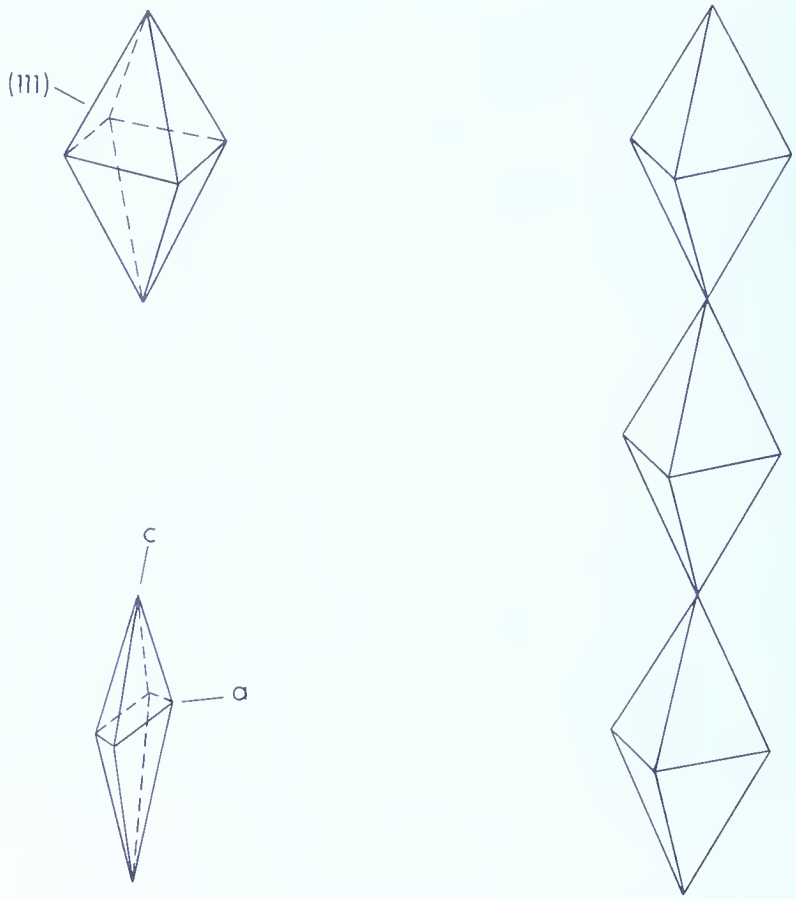

Figure 18. Orthorhombic sulfur crystals.

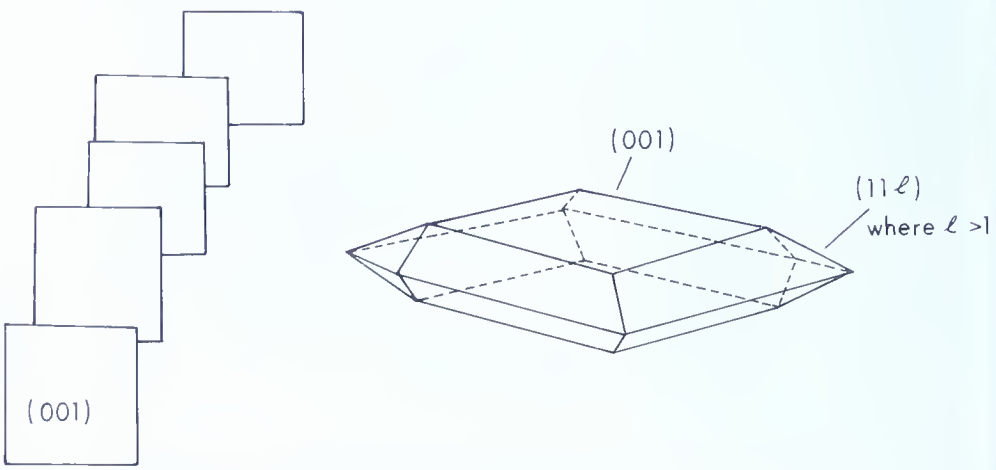

Figure 19. Orthorhombic sulfur displaying large (001) faces.

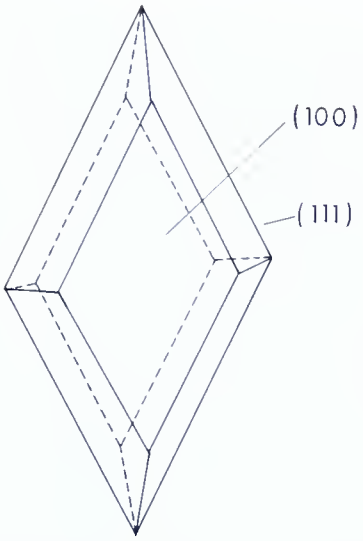

Figure 20. Thin orthorhombic dipyramid of sulfur.

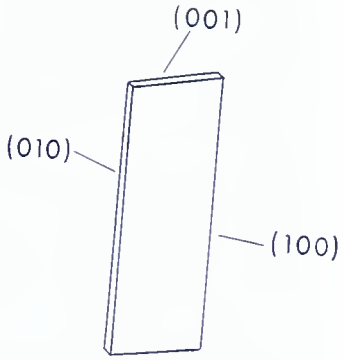

Figure 21. Elongate lath of sulfur believed to be monoclinic.

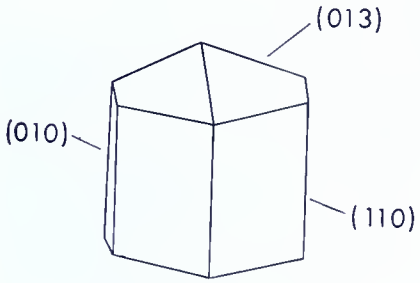

Figure 22. Sulfur form observed on waste piles and not noted previously.

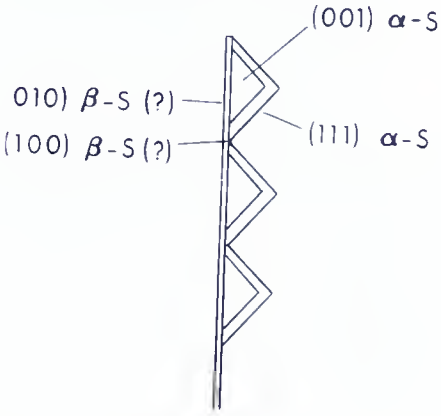

Figure 23. Sulfur crystals, involving monoclinic and orthorhombic forms, similar to forms observed on burning waste piles (after Goldschmidt, 1922, Tafeln, v. 8, Tafel 22).

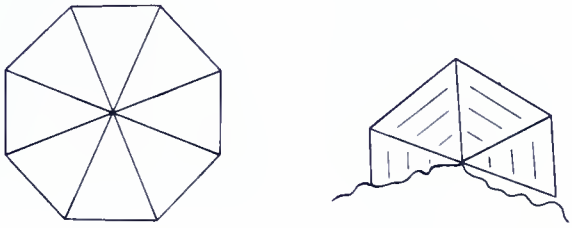

Figure 24. Sulfur crystals believed to be cyclic twins.

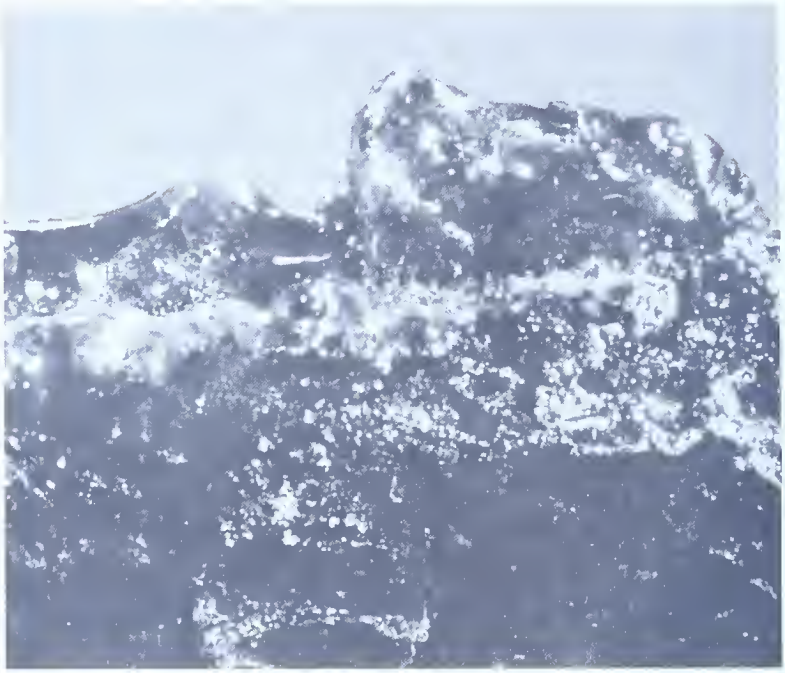

Figure 25. Red glassy material, probably an amorphous mixture of sulfur and selenium.

Figure 26. Skeletal aggregates of sulfur crystals from Glen Lyon. Flat plates are approximately 2 mm (0.08 in.) wide.

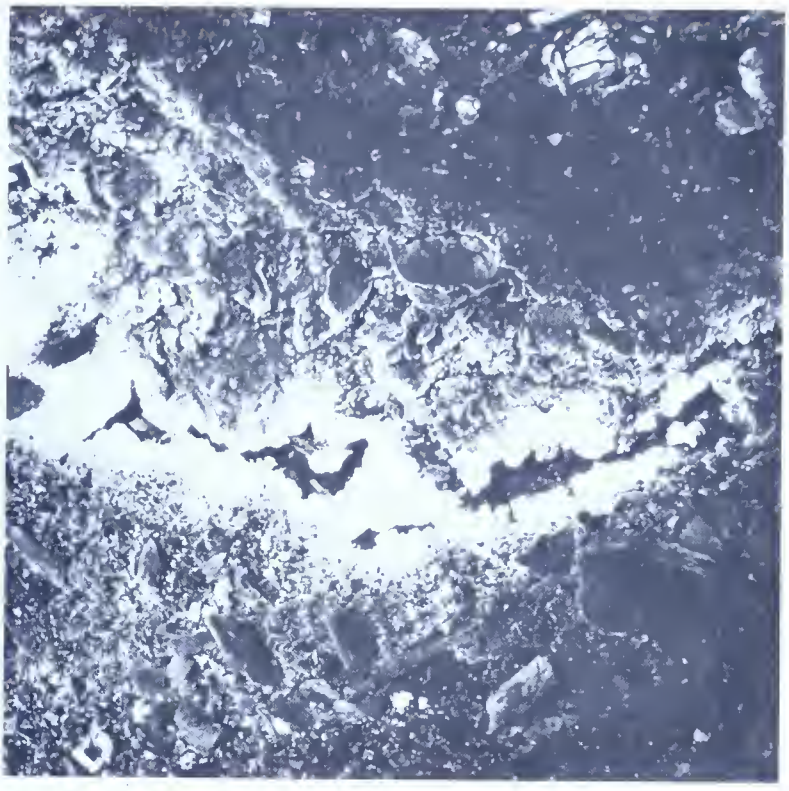

Figure 27. Sulfur crystals surrounding vents on the surface of the waste pile at Glen Lyon. Length of vent is approximately 30 cm (12 in.).

centimeters to a meter (1 in. to 3 ft) in diameter, around many vents (Figure 27). The largest crystals, up to 3 cm (1.2 in.) long, are found in areas protected from wind and precipitation. At Forestville, layers of sulfur crystals extending over several square meters (several tens of square feet) were found 10 to 20 cm (4 to 8 in.) below the surface. Pools of liquid sulfur (M.P. = 112.8°C, or 235.1°F) and masses of resolidified sulfur were found on the waste piles (Figure 28). All sulfur subjected to X-ray diffraction was orthorhombic, indicating that the externally monoclinic forms observed were pseudomorphs that originally crystallized in the monoclinic system between the melting point of monoclinic sulfur (119°C, or 246.2°F) and the temperature of transition to orthorhombic sulfur (95.5°C, or 203.9°F; Garrels and Christ, 1965, p. 334).

Associations: All other observed minerals except most occurrences of oxides, sulfides, and sulfates. One small sample of mascagnite contained sulfur crystals. Reddish "sulfur" crystals near selenium probably are "selen-sulfur."

Origin: Sublimation.

Identification: Color, habit, crystallography, X-ray diffraction.

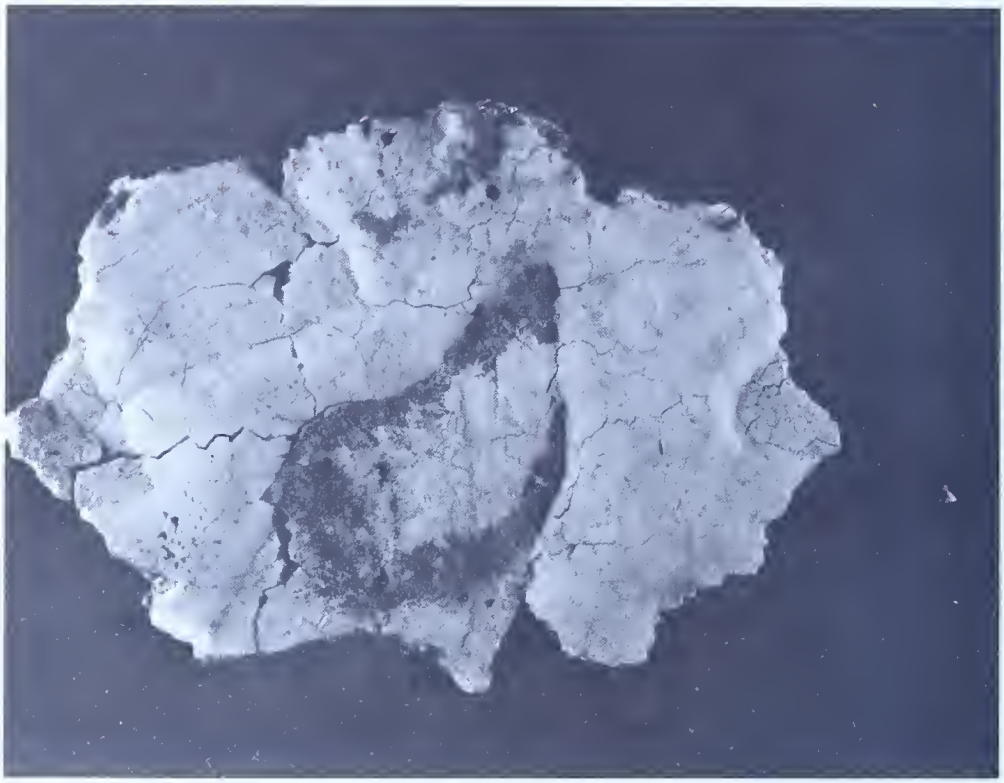

Figure 28. Sulfur that has been melted and resolidified, from Forestville.

SULFIDES AND SELENIDES

Galena

Formula: PbS
System: Cubic
Habit: Dark-gray microscopic cubic crystals (Figure 29), iridescent coating.
Occurrence: Kehley's Run mine and Burnside, incrusting higher temperature vents (>320 °C, or >608 °F).
Associations: Cassiterite.
Origin: Sublimation. Such an occurrence has been reported from volcanic fumaroles (Lindgren, 1933, p. 113).
Identification: Color, morphology, X-ray diffraction.

Pyrrhotite

Formula: $Fe_{1-x}S$
System: Hexagonal
Habit: Bluish iridescent hexagonal prisms. Some skeletal crystals (Figure 30).

Figure 29. Scanning-electron photomicrograph of galena (tiny cubes) on cassiterite from Burnside. Bar scale is 10 μm (0.0004 in.).

Occurrence: Burnside.
Associations: None observed.
Origin: Probably a sublimate. Has been synthesized by heating pyrite in an atmosphere of H_2S at 550°C (1022°F) (Palache and others, 1944).
Identification: X-ray diffraction, energy-dispersive X-ray analysis.

Realgar

Formula: AsS
System: Monoclinic
Habit: Flattened prismatic orange-red monoclinic crystals approximately 2 mm (0.08 in.) in length.
Occurrence: On the upper surfaces of small cavities just below the surface of the Glen Lyon waste pile, at observed temperatures ranging from 90 to 140°C (194 to 284°F) (minimum range of formation). The maximum temperature of formation could not have exceeded 250 to 260°C (480 to 500°F) (Hall, 1966; Roland, 1966), above which α-AsS forms. Alpha-AsS

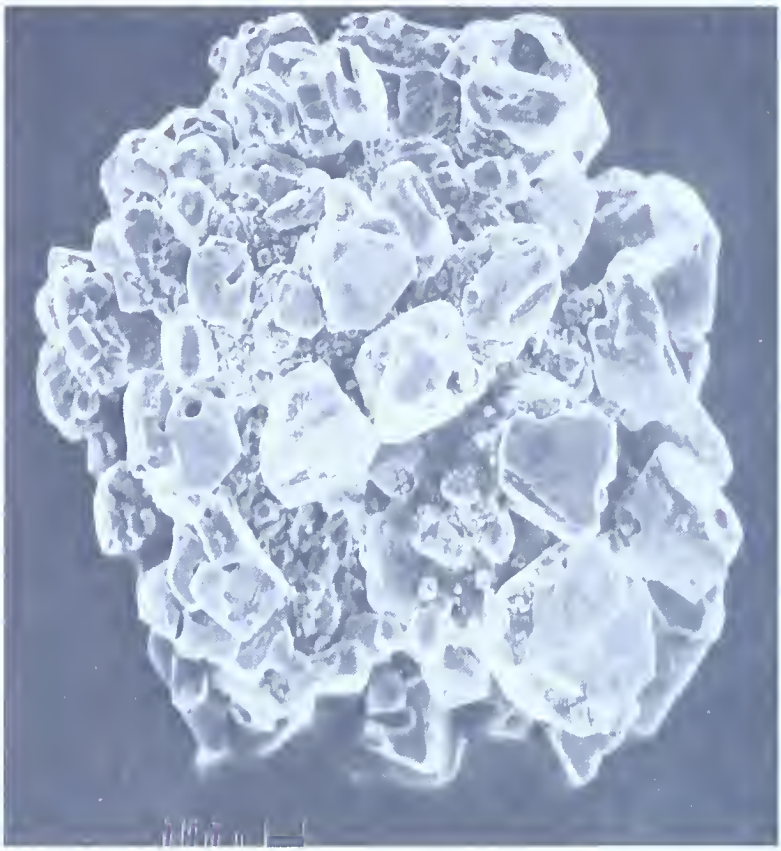

Figure 30. Scanning-electron photomicrograph of pyrrhotite from Burnside. Bar scale is 10 μm (0.0004 in.).

is metastable at temperatures as low as 25°C (77°F) for a minimum of 2 years (Clark, 1970), but was not detected.

Associations: Cryptohalite, selenium, possible GeS_2. Sulfur was present on the surface above the cavities. No orpiment was observed at Glen Lyon, and none appears to have formed after 7 years of light-tight storage.

Origin: Probably sublimation.

Identification: X-ray diffraction, color, morphology. A semiquantitative emission-spectrographic analysis indicated major As and Ge; minor Si, Sb, and Fe; and trace Cu, Mg, Mn, and Al.

Herzenbergite

Formula: SnS

System: Orthorhombic

Habit: Irregular black plates.

Occurrence: Forestville.

Associations: Berndtite.

Origin: Probably by direct sublimation. Herzenbergite is known from three other locations, all foreign (Moh, 1969). The source of the tin is problematical. The abundance of tin in coal is generally less than one part per million (Zubovic and others, 1966); however O'Gorman (1971) found more than 4,000 ppm in low-temperature ash nearby at Zerbe.
Identification: X-ray diffraction and electron microprobe.

Orpiment

Formula: As_2S_3
System: Monoclinic
Habit: Yellow to orange clusters of radiating crystals. Darker colors may be from admixed selenium.
Occurrence: Burnside.
Associations: Sulfur, arsenolite, and As_2Se_3.
Origin: Probably a sublimate.
Identification: X-ray diffraction, energy-dispersive X-ray analysis.

Arsenic Selenide

Formula: As_2Se_3
System: Monoclinic
Habit: Dark-red radiating clusters of tabular crystals up to 3 mm (0.1 in.) long.
Occurrence: Burnside.
Associations: Arsenolite and orpiment. Appears to form a complete solid-solution series with As_2S_3.
Origin: Probably by sublimation.
Identification: X-ray diffraction, energy-dispersive X-ray analysis, quantitative electron-microprobe analysis. Powder-diffraction data compared to that of synthetic material. Further study is in progress.

Bismuthinite

Formula: Bi_2S_3
System: Orthorhombic
Habit: Black shiny needles, up to 1 mm (0.04 in.) in length.
Occurrence: Forestville.
Associations: Berndtite, $KAlF_4$, $KAl(SO_4)_2$, and an unidentified aluminosilicate.
Origin: Hollow crystals (Figure 31) are a good indication of an origin by direct sublimation.
Identification: X-ray diffraction and energy-dispersive X-ray analysis.

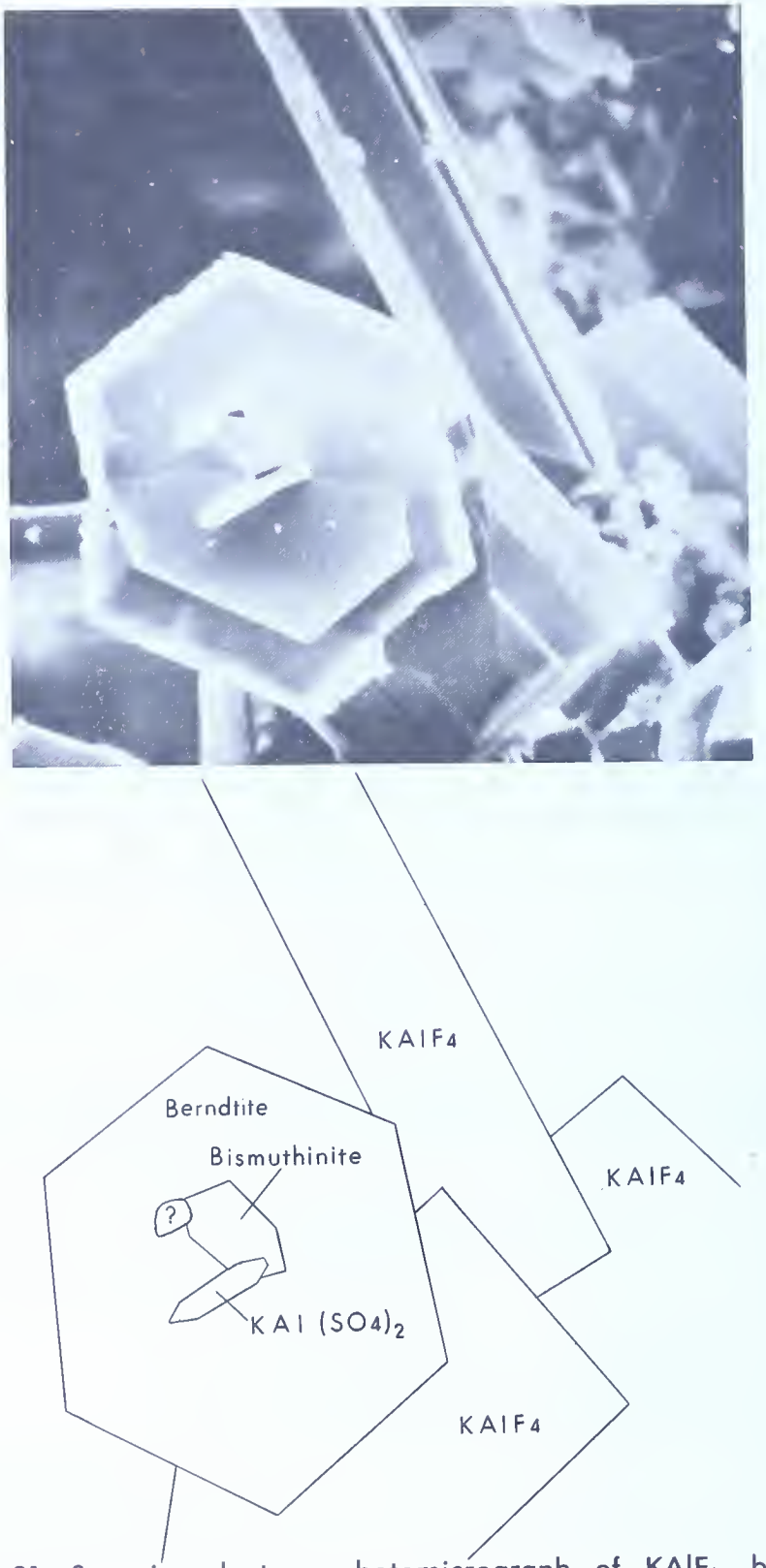

Figure 31. Scanning-electron photomicrograph of $KAlF_4$, berndtite, bismuthinite, and $KAl(SO_4)_2$ from Forestville.

Ottemannite

Formula: Sn_2S_3
System: Orthorhombic
Habit: Very thin, blue iridescent plates up to several millimeters (about 0.1 in.) in length, or brittle networks of shiny black needles.
Occurrence: Forestville.
Associations: GeS_2, berndtite, and $KAlF_4$.
Origin: Probably by direct sublimation. Ottemannite has been reported from only two other locations, both foreign (Moh, 1969). See herzenbergite for comments on the source of the tin.
Identification: X-ray diffraction and electron microprobe.

Berndtite

Formula: SnS_2
System: Hexagonal
Habit: Bright-yellow thin hexagonal plates (Figure 31) on selenium, $KAlF_4$, and bismuthinite.
Occurrence: Found in very small quantity on one specimen from Forestville.
Associations: Selenium, $KAlF_4$, ottemannite, herzenbergite, and bismuthinite.
Origin: Delicate, well-formed crystals indicate that berndtite formed by direct sublimation. See herzenbergite for comments on the source of the tin. Berndtite has been reported from three other locations, all foreign (Moh, 1969; Clark, 1969).
Identification: X-ray diffraction, electron microprobe, and physical properties.

Germanium Sulfide

Formula: GeS_2
System: Orthorhombic
Habit: Small tufts (approximately 1 mm, or 0.04 in.) of radiating white fibers, having a brownish tint near the top, on an ottemannite substrate. Each fiber is a smooth rod (approximately 100 μm (0.004 in.) long, 5 μm (0.0002 in.) wide) capped by a small bulb of amorphous sulfur. The rods often have many smaller bulb-tipped rods projecting as perpendicular branches (Figure 32).
Occurrence: Found rarely at the opening of a vent at Forestville.
Associations: Ottemannite and amorphous sulfur.
Origin: Believed to be the first naturally occurring terrestrial example of the vapor-liquid-solid (VLS) growth mechanism (Finkelman, Larson, and Dwornik, 1974). This mechanism, as described by Wagner and Ellis

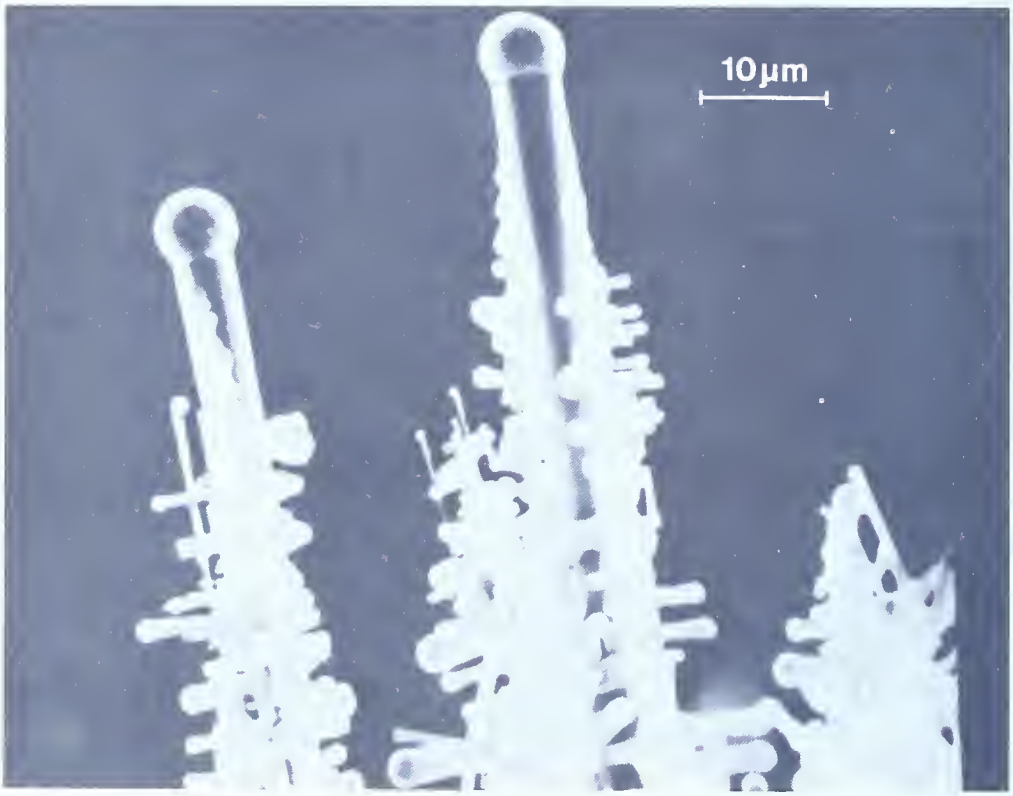

Figure 32. Scanning-electron photomicrograph of GeS_2 crystals from Forestville. The largest rods are approximately 100 μm (0.004 in.) long and 5 μm (0.0002 in.) wide.

(1964), typically involves the formation at elevated temperature of a droplet of a liquid alloy on a solid substrate (Figure 33a). The liquid droplet acts as a catalyst for the condensation of elements from surrounding vapors. The elements from the vapor enter the liquid, supersaturating it, then precipitate out of the base of the droplet to form the elongated crystals (Figure 33b). The droplet capping the growing crystal eventually solidifies to form the distinctive bulb.

Identification: X-ray diffraction, electron diffraction, electron microprobe, energy-dispersive X-ray analysis. The last method also detected the presence of variable quantities of tin, perhaps as a thin coating of one of the tin sulfides. Powder-diffraction data were compared with data for synthetic material. Further study of this unnamed species is in progress.

OXIDES

Hematite

Formula: Fe_2O_3
System: Trigonal

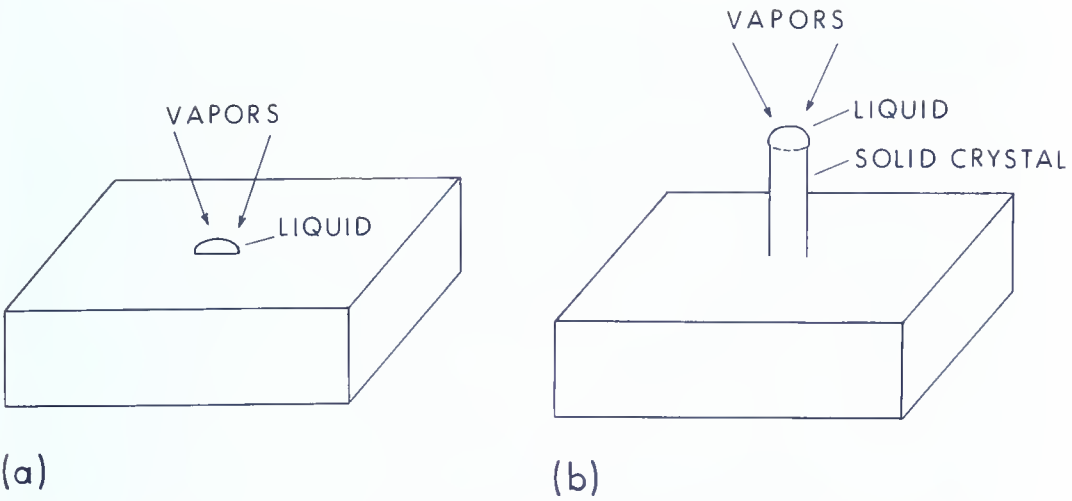

Figure 33. Illustration of the vapor-liquid-solid growth mechanism. (a) A liquid droplet forms by condensation on a solid substrate. The droplet begins to act as a catalyst for the condensation of elements from surrounding vapors. (b) Elements from the vapor supersaturate the liquid, then precipitate out to form an elongated crystal with the liquid droplet perched on top. The droplet eventually solidifies to form an amorphous bulb (after Wagner and Ellis, 1964).

Habit: Most has a reddish-ochre color and is present mainly as a coating and matrix material in rocks. Minor amounts of specular and compact columnar hematite were observed, exhibiting a range of crystal morphology from cubes to what appears to be a type of VLS growth (see GeS_2). It is possible that the hematite is pseudomorphous after magnetite. Some observations indicated that the material is slightly magnetic, perhaps owing to unaltered magnetite or maghemite.

Occurrence: Present at all banks. The specular and columnar varieties were observed at Kehley's Run mine and Williamstown.

Association: Mullite.

Origin: Intimate association of specular hematite with mullite at Williamstown (Figure 34) suggests a very high temperature of formation, perhaps in the interior of the bank. Oxidation of other iron minerals, such as pyrite, as a consequence of the fire is most likely. Iron-bearing minerals are common constituents of coal.

Identification: X-ray diffraction, color, habit.

Arsenolite

Formula: As_2O_3

System: Cubic

Habit: Octahedral crystals (Figure 35).

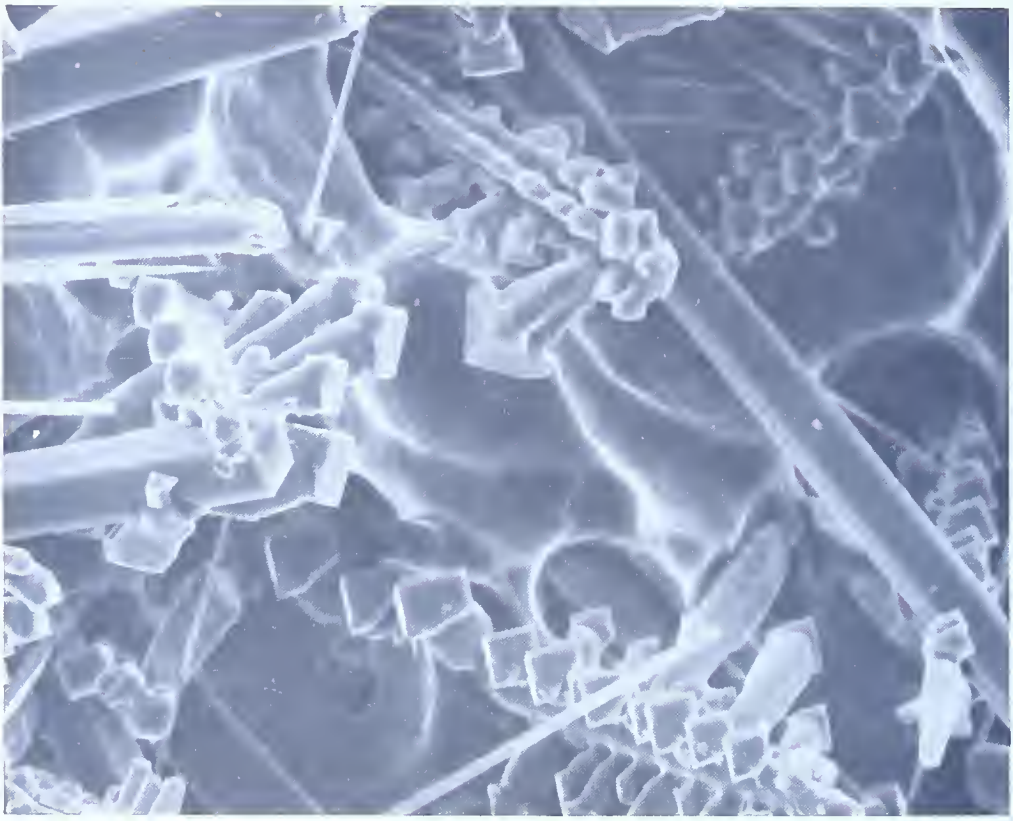

Figure 34. Scanning-electron photomicrograph of hematite and mullite from Williamstown.

Occurrence: Burnside.
Associations: Orpiment and As_2Se_3.
Origin: Probably a sublimate. Higher temperature regime than nearby orpiment.
Identification: X-ray diffraction, energy-dispersive X-ray analysis.

Cassiterite

Formula: SnO_2
System: Tetragonal
Habit: Gray to dark-brownish-gray tabular crystals having pyramidal terminations (Figures 29 and 36). Approximately 1 mm (0.04 in.) in length by ½ mm (0.02 in.) in width. Many are slightly curved, the axis of curvature being parallel to the C axis.
Occurrence: Clusters of crystals lining cavity 8 to 10 cm (3 to 4 in.) below surface of Forestville waste pile. Also found at Burnside.
Associations: Berndtite, ottemannite, herzenbergite, $KAlF_4$, GeS_2, $KAl(SO_4)_2$, potassium alum, and bismuthinite at Forestville. Sulfur was on the surface above the cavity. Associated with galena at Burnside.

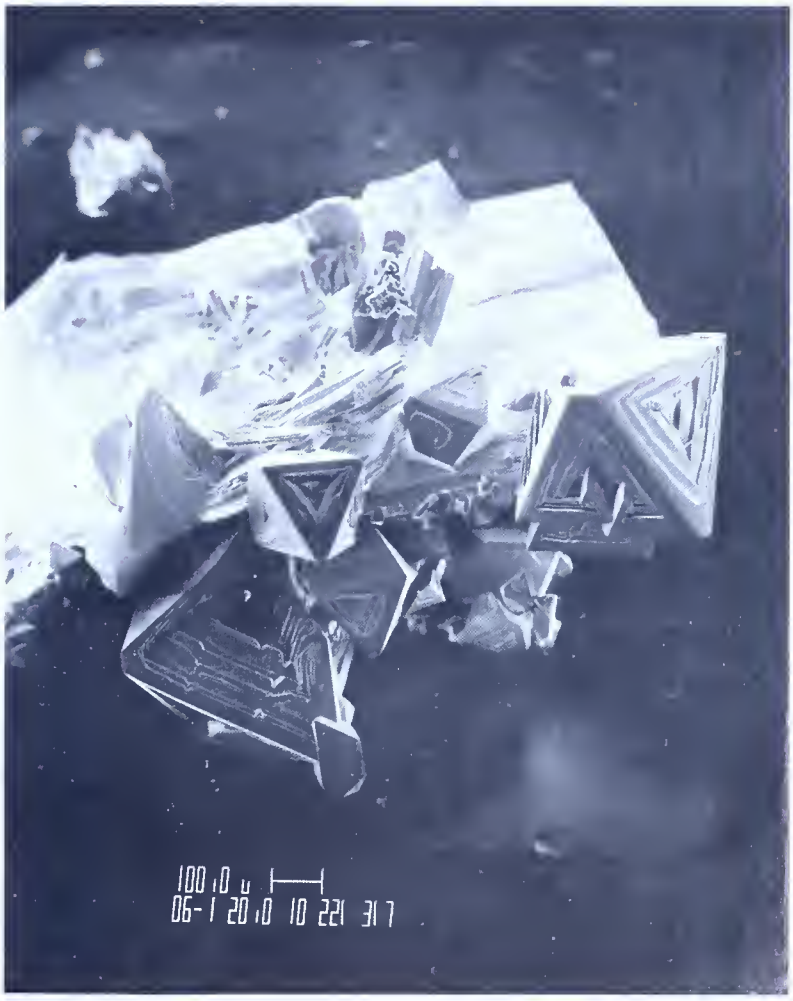

Figure 35. Scanning-electron photomicrograph of arsenolite octahedra from Burnside. Bar scale is 100 μm (0.004 in.).

Origin: The habit and mode of occurrence indicate a relationship to vapor-deposited material. Perhaps the cassiterite is an alteration product of the various vapor-deposited tin sulfides. Cassiterite is normally considered a high-temperature mineral (see, for example, Palache and others, 1944); however, Pan and Ypma (1974) demonstrated that low-temperature genesis of cassiterite is possible.

Identification: X-ray diffraction.

Downeyite

Formula: SeO_2

System: Tetragonal

Habit: Transparent colorless prismatic crystals having adamantine luster (Figure 37). Individual needles range from 0.1 mm to 2 cm (0.004 to 0.8 in.) in length.

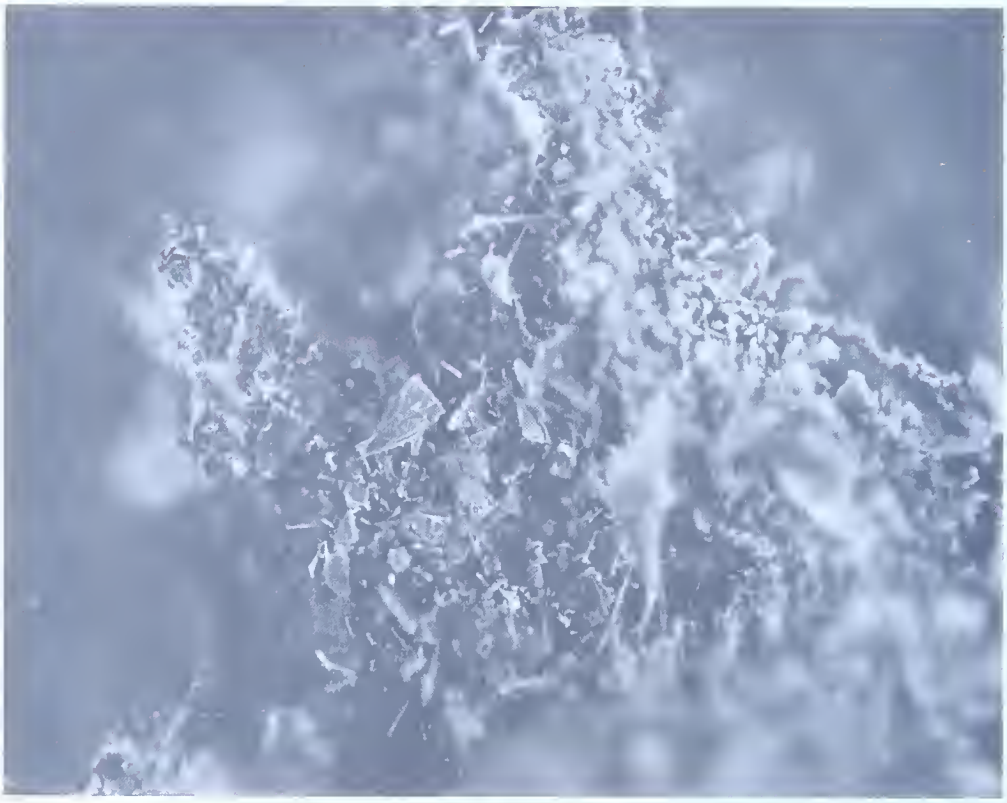

Figure 36. Cassiterite crystals from Forestville. Individual crystals are 1 to 2 mm (0.04 to 0.08 in.) long.

Occurrence: Found sparingly as individual crystals or radiating clusters on waste piles at Forestville, Glen Lyon, Williamstown, and Burnside. Temperatures in the zones in which these crystals were found were generally in the range 190 to 230°C (374 to 446°F). The crystals are extremely hygroscopic and unstable under normal atmospheric conditions. As soon as they are removed from the hot, dry environment in which they form, they quickly absorb water from the atmosphere and, in a few minutes, deliquesce, leaving droplets of a clear, colorless liquid which either evaporates or is absorbed into the porous substrate.

These occurrences are the first verified natural occurrences of SeO_2 to be recognized.

> The name selenolite has been used for minerals assumed to be SeO_2. The descriptions of these minerals indicate that none could have had this composition. Therefore, the name selenolite. . .[was] rejected in favor of the name downeyite for this. . .mineral. The name is for [the discoverer] Wayne F. Downey, Jr. . . . (Finkelman and Mrose, 1977, p. 316)

Associations: Downeyite appears to have formed simultaneously with selenium in association with sulfur, mascagnite, and anhydrous aluminum sulfate. Some downeyite crystals appear red because of inclu-

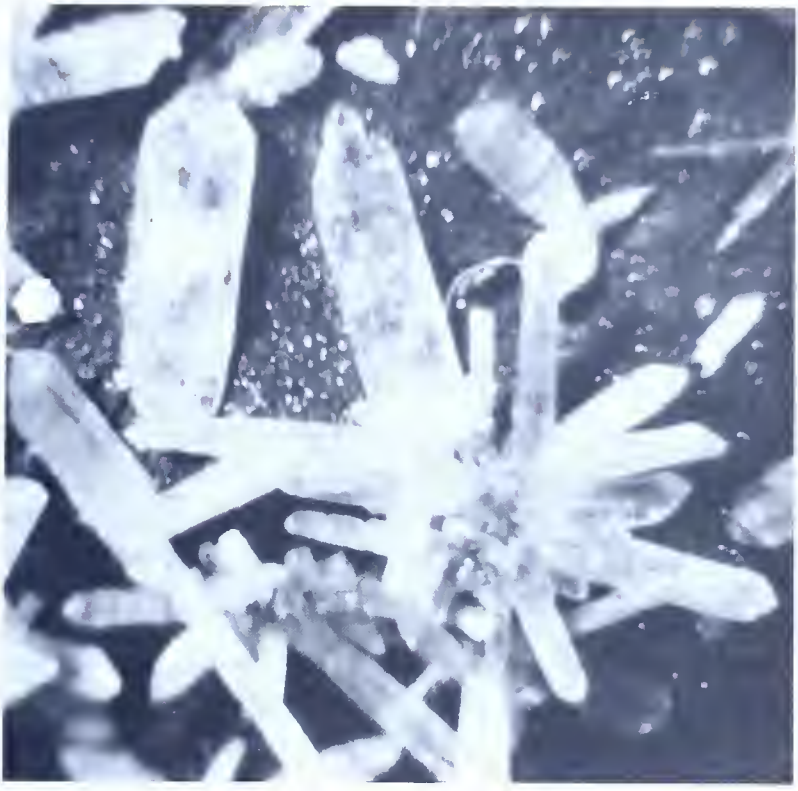

Figure 37. Downeyite crystals from Glen Lyon.

sions of amorphous selenium. Others have a dusting of sulfur, giving them a yellowish tint. Some selenium crystals had droplets of a clear, colorless liquid on them which is quite likely the residue of downeyite.

Origin: Probably by direct sublimation. Synthetic SeO_2 is reported to sublime at about 350 °C (662 °F).

Identification: X-ray diffraction, energy-dispersive X-ray analysis, electron microprobe, and physical properties (see Finkelman and Mrose, 1977).

HALIDES

Salammoniac

Formula: NH_4Cl

System: Cubic

Habit: Mostly white incrustations of clear, colorless, stalactitic and skeletal cubic and dodecahedral crystals which range from 1 to 10 mm (0.04 to 0.4 in.) in length. Some crystals have step-growth faces, some others are curved, and many are lightly etched. Most crystals appear turbid in oil immersion and have a refractive index of 1.639 ± .001. Crystals from one sample were clear in oil immersion, required only slight pressure with a

point probe to be deformed by crystal gliding, and yielded a shift in the powder-diffraction pattern (Table 3). The unit-cell-edge length (a_0) for this material was 3.912Å, as opposed to 3.87Å for "normal" salammoniac from the same location and 3.8756Å calculated by Swanson and Tatge (1953, p. 59) for synthetic NH_4Cl. Several rare samples had an orange coloration, and one consisted of a mammillary, botryoidal crust exhibiting contraction cracks and green fluorescence in shortwave ultraviolet light.

Occurrence: Common at Kehley's Run mine, in protected areas under rocks and in and around vents. Not verified elsewhere. Usually found in areas where the temperature was about 200°C (390°F), although salammoniac sublimes at 340°C (644°F) (Weast, 1972, p. B-65). The minimum time for crystallization was measured as less than 24 hours.

Associations: Cryptohalite, bararite, sulfur, and mascagnite. A diffuse X-ray diffraction band centered at about 4.2Å and the green fluorescence suggest the presence of opal in the botryoidal specimen. Cryptohalite, sulfur, and salammoniac usually occupy well-defined zones on each sample.

Origin: Sublimation. The abundance at Shenandoah and lack at other locations is paralleled by $(NH_4)_2SiF_6$ (cryptohalite and bararite); however, other areas have abundant ammonium sulfates that are much less common at Shenandoah. Whether this is the result of differences in the amount of halogens or differences in other factors such as temperature or solution could not be ascertained.

Identification: X-ray diffraction, physical properties.

Potassium Aluminum Fluoride

Formula: $KAlF_4$

System: Tetragonal

Habit: Transparent colorless lathlike crystals generally about 100 μm (0.004 in.) wide, although some exceed 1 mm (0.04 in.) in length. Scanning-electron microscopy reveals a great variety of well-formed rhombic prisms, many having intricately stepped faces (Figures 31 and 38). Twinning appears to be fairly common.

Occurrence: Found at Forestville on two separate occasions. These delicate, well-formed crystals were perched on the rubbly surface of the waste pile.

Associations: Found with berndtite and bismuthinite, and intimately associated with $KAl(SO_4)_2$.

Origin: The small, delicate, perfectly formed crystals are best explained as a direct sublimate.

Identification: X-ray diffraction and electron microprobe. Powder-diffraction data compared to that of synthetic material. Further study is in progress.

Table 3. *X-ray Powder Diffraction Data for Salammoniac*

	1		2		3	
hkl	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
100	3.87	25	3.88	30	3.92	30
110	2.740	100	2.74	100	2.77	100
111	2.238	4	2.24	10	2.26	10
200	1.939	8	1.93	20	1.95	15
210	1.733	6	1.73	15	1.75	12
211	1.582	25	1.58	40	1.60	20
220	1.370	6	1.37	12	1.38	6
300	1.292	4	1.29	10	1.31	5
310	1.225	6	1.23	15	1.24	4
311	1.1687	4	1.17	8		
222	1.1188	2	1.12	5	1.13	1
320	1.0751	2	1.07	3		
321	1.0357	4	1.04	15	1.04	2

1. Synthesized ammonium chloride (Swanson and Tatge, 1953, p. 59).
2. "Normal" salammoniac from Shenandoah, Pennsylvania. Intensities determined by visual estimate.
3. Salammoniac from Shenandoah exhibiting crystal gliding. Intensities determined by visual estimate.

Figure 38. Scanning-electron photomicrograph of $KAlF_4$ crystals from Forestville.

Cryptohalite

Formula: $(NH_4)_2SiF_6$

System: Cubic

Habit: Usually clear, colorless, tabular crystals that are commonly etched or skeletal; and interpenetrating crystal groups about 1 mm (0.04 in.) across (Figure 39). Some samples consist of intergrown aggregates forming columns approximately 2 mm (0.08 in.) in length, topped by a minute gray metallic spheroid in a cavity at the top of each column (Figure 16). Some crystals have a red coating.

Occurrence: In protected areas under surface material, and, in smaller amounts, lining vents and on the surface, at Kehley's Run mine and at Glen Lyon. Observations at Kehley's Run mine indicate that cryptohalite crystals can form through sublimation in less than 24 hours.

Associations: Most crystals contain inclusions of bararite. Most samples from Kehley's Run mine contain salammoniac and sulfur in overlapping and gradational zones. At Glen Lyon it is generally in close proximity to sulfur and selenium. The red coating on some cryptohalite crystals from

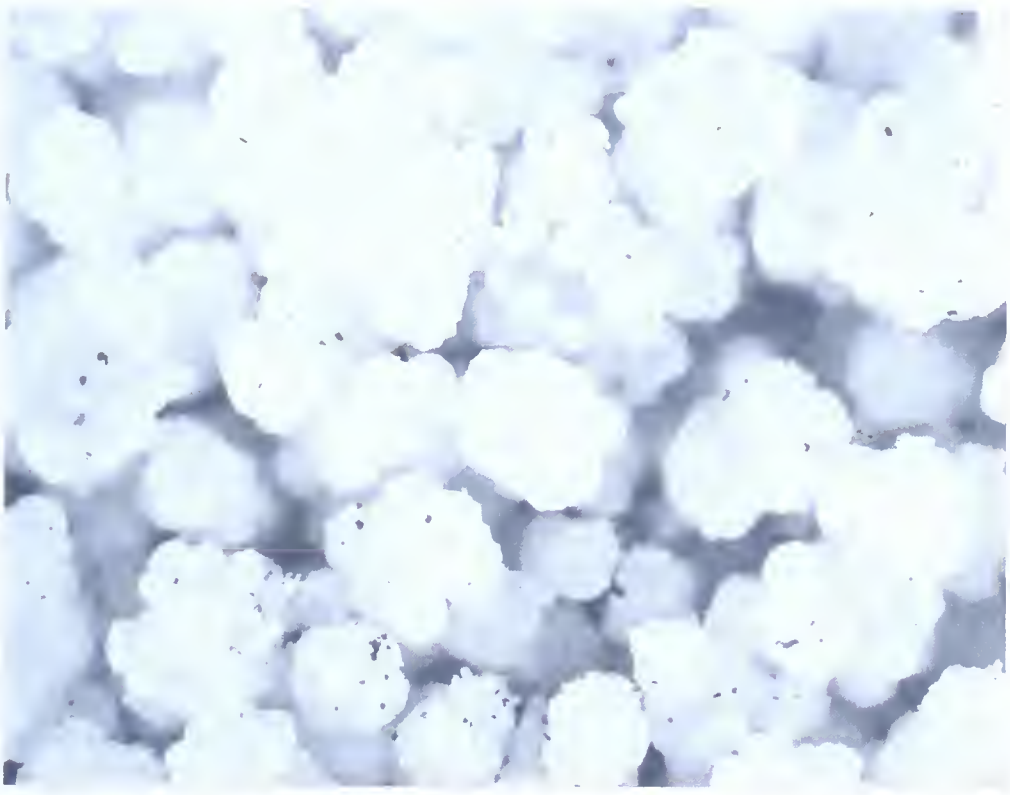

Figure 39. Rounded groups of interpenetrating crystals of cryptohalite from Glen Lyon. Each group is approximately 1 mm (0.04 in.) across.

Glen Lyon and the metallic spheroids that top the columns of cryptohalite are both amorphous to X-rays, but probably consist of selenium.

Origin: Indirectly by sublimation, probably by the alteration of bararite.

Identification: X-ray diffraction, physical properties.

Bararite

Formula: $(NH_4)_2SiF_6$

System: Hexagonal

Habit: Inclusions in cryptohalite crystals which are visible only in transmitted plane-polarized light by their anisotropy in the isotropic cryptohalite. The inclusions are elongated parallel to the direction of elongation of the cryptohalite and have low birefringence and low relief. In grains containing more than one inclusion, all are optically aligned.

Occurrence: Kehley's Run mine; probably also at Glen Lyon waste pile.

Associations: All observed bararite was contained within cryptohalite grains.

Origin: Sublimation. The optical alignment of bararite inclusions in each cryptohalite grain suggests that bararite forms first by direct sublimation, then quickly alters to cryptohalite. Christie (1926, p. 235) hypothesized that fluorine, probably released from fluoride minerals by sulfur dioxide, would react with silicate minerals to form silicon fluoride, which is stable as a gas down to −18.5 °C (−1.3 °F). The silicon fluoride would, in turn, react with ammonia from the anthracite to form $(NH_4)_2SiF_6$.

Identification: X-ray diffraction and optical properties. Standard powder-diffraction data for bararite were not available, and a pattern was calculated by analogy with $(NH_4)_2GeF_6$ using $a_0 = 5.77$Å, $c_0 = 4.78$Å (Gossner and Kraus, 1934, p. 488) (Table 4).

SULFATES

Mascagnite

Formula: $(NH_4)_2SO_4$

System: Orthorhombic

Habit: Most commonly as a white earthy powder, intermixed with other sulfates. Also as delicate white feathery and fernlike aggregates of crystals, the aggregates ranging from 1 to 5 mm (0.04 to 0.2 in.) in length (Figure 40); individual transparent, colorless needles approximately 1 to 2 mm (0.04 to 0.08 in.) long; and rarely as "spire-like" pale-yellow needles 2 to 3 mm (0.08 to 0.12 in.) long. The smallest of the orthorhombic crystals in fernlike aggregates, when viewed in a transmitted-light microscope, are transparent and colorless, whereas the larger crystals are somewhat complex and turbid, probably because of inclusions and cavities. The crystals studied were elongated parallel to the b axis, using the arbitrarily assigned axes of Taylor and Boyer (1928). Some crystals exhibited steplike growth of certain faces, and many face intersections are indeterminate, appearing rounded.

Occurrence: The earthy powder was found at the Glen Lyon and Williamstown waste piles. All other forms observed were on samples from Kehley's Run mine.

Associations: The earthy powder is an intimate mixture of tschermigite, $NH_4Al(SO_4)_2$, and mascagnite. The other forms were pure, within limits of detection. The "spire-like" needles were proximal to cryptohalite, salammoniac, sulfur, and several unidentified compounds.

Origin: Probably by sublimation. Mascagnite is a common condensate at areas of fumarolic activity.

Identification: X-ray powder diffraction and refractive indices ($\alpha = 1.520 \pm .002$, $\beta = 1.523 \pm .002$, $\gamma = 1.53 \pm .01$). Winchell and Benoit (1951, p. 592) presented three rather different powder-diffraction patterns for mascagnite. In this study, all but one of the samples match patterns for

Table 4. X-ray Powder Diffraction Data for Bararite

1		2		3		4	
d(Å)	I/I_1	d(Å)	hkl	d(Å)	I/I_1	d(Å)	I/I_1
5.00	20	5.017	100				
4.84	100	4.778	001	4.844	100		
4.20	20			4.195	25		
3.88	5					3.87	25
3.45	30	3.456	101				
3.29	2						
3.04	<1						
2.96	15			2.967	18		
2.88	1	2.889	110				
2.74	20					2.740	100
2.53	3			2.531	8		
		2.472	111				
2.42	45			2.422	45		
		2.389	002				
2.32	<1						
2.22	35	2.216	201			2.238	4
		2.156	102				
2.09	40			2.098	35		
1.93	5			1.926	4	1.939	8
		1.891	210				
				1.877	4		
		1.841	112				
1.75	1	1.758	211				
1.73	6	1.728	202			1.733	6
		1.668	300				
1.61	15	1.593	003	1.615	18		
1.58	5	1.575	301			1.582	25
		1.518	103				
1.48	10	1.483	212	1.4837	8		

1. Observed pattern, sample from Kehley's Run Mine, Shenandoah, Pennsylvania. Intensities determined by visual estimate.
2. Calculated bararite pattern, using $a_0 = 5.77$A, $c_0 = 4.78$A (Gossner and Kraus, 1934, p. 488).
3. Cubic $(NH_4)_2SiF_6$ (cryptohalite) (Swanson and others, 1955, p. 5).
4. NH_4Cl (salammoniac) (Swanson and Tatge, 1953, p. 59).

Figure 40. Aggregates of mascagnite from Glen Lyon.

synthetic $(NH_4)_2SO_4$ quoted by Winchell and Benoit and published by Swanson and others (1960, p. 9). They also match the pattern the authors obtained for mascagnite formed by sublimation above a burning coal seam at Commentry, France (Table 5). One sample from Glen Lyon matched a different "mascagnite" pattern obtained by Winchell and Benoit from sample 1693 in the Brush Collection, Yale University, collected from The Geysers, Sonoma County, California. A third "mascagnite" pattern, obtained by Winchell and Benoit from material from Mt. Vesuvius, was not observed in this study. Material from The Geysers was originally identified as "mascagnite" by unspecified means by Vonsen (1946) and Switzer (1951). The purpose of Winchell and Benoit's study was the collection of standard powder-diffraction data for sulfates. Because of the disagreement, it appears that the name "mascagnite" has been applied to three different materials. Based on their agreement with synthetic material, most of the authors' samples, and that from Commentry, are certainly orthorhombic $(NH_4)_2SO_4$, as mascagnite is defined (Fleischer, 1975, p. 74). The authors' sample that was in agreement with Winchell and Benoit's data from material from The Geysers was intermixed with tschermigite and $NH_4Al(SO_4)_2$, and consequently was not of

Table 5. *X-ray Powder Diffraction Data for Mascagnite*

	1		2		3*		4		5	
d(A)	I/I_1	hkl	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
							5.44	10		
5.31	15	002			5.35	20				
5.22	30	011	5.25	15	5.20	20				
							4.96	90	4.94	50
							4.65	30	4.64	20
4.33	100	111	4.35	100	4.36	80	4.31	40	4.34	30
3.90	35	200	3.89	40	3.88	100				
							3.74	80	3.78	15
3.66	<1	201								
							3.36	100	3.36	100
3.26	<1	210								
3.23	2	103			3.21	6				
3.14	30	202			3.13	25				
3.12	25	211	3.12	35						
3.06	55	013	3.04	30	3.05	14	3.04	10		
2.998	25	020	2.98	10	3.00	6				
							2.90	70	2.91B	350†
2.839	2	113								
2.782	4	212	2.78	2						
2.704	6	121	2.71	2						
							2.68	10		
2.655	14	004	2.66	15	2.66	5				
2.611	8	022	2.61	1						
2.521	10	301	2.52	20	2.52	2				
2.476	4	122	2.48	<1			2.48	30	2.46	10

Table 5. *(Continued)*

	1		2		3*		4		5	
d(A)	I/I_1	hkl	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
2.401	4	213								
2.374	4	220	2.38	2						
2.322	18	311	2.32	25	2.32	8	2.32	10		
2.317	20	221								
2.196	10	132, 204	2.20	8			2.20	20	2.18B	10
2.168	16	222	2.16	12	2.17	5				
2.093	6	303			2.10	2				
2.062	<1	214								
2.005	<1	015								
1.973	6	223								
1.945	6	400								
1.942	6	115								
1.927	<1	321, 124								
1.914	4	401								
							1.884	10	1.87	2

1. Synthetic $(NH_4)_2SO_4$, Johnson Matthey and Co., London, England (Swanson and others, 1960, p. 9).
2. Mascagnite collected at Glen Lyon waste pile. Intensities determined by visual estimate.
3. Mascagnite from burning coal seam at Commentry, France (sample from the museum of l'Ecole Nationale Supérieure des Mines, Paris). Intensities determined by visual estimate.
4. "Mascagnite" from The Geysers, Sonoma County, California (sample 1693, Brush Collection, Yale University) (Winchell and Benoit, 1951, p. 592).
5. Mascagnite-like material collected at Glen Lyon waste pile. Intensities determined by visual estimate. B = broad.

*Powder-diffraction pattern indicates salammoniac as main constituent, minor quartz, mica, possible kaolinite.

†Intensity enhanced by $NH_4Al(SO_4)_2$ at 2.92 Å.

high enough purity to make further testing possible. It may be a chemical variant, a polytype, or a different compound, but probably neither it, nor material from The Geysers, should presently be referred to as "mascagnite."

Potassium Aluminum Sulfate

Formula: $KAl(SO_4)_2$
System: Tetragonal
Habit: Transparent, colorless lathlike crystals, morphologically identical to those of $KAlF_4$ (Figure 31). Also white branching rods, each branch no more than 1 or 2 mm (0.04 to 0.08 in.) in length.
Occurrence: Found at Forestville at two separate locations.
Associations: The transparent, colorless variety is intimately associated with $KAlF_4$. The white branching rods were found in association with cryptohalite and sulfur.
Origin: Probably direct sublimation. Has been found at volcanic vents by Stoiber and Rose (1974).
Identification: X-ray diffraction and electron microprobe. Powder data compared to that of synthetic material.

Ammonium Aluminum Sulfate

Formula: $NH_4Al(SO_4)_2$
System: Hexagonal
Habit: Commonly as an earthy white compact powder. Also as yellowish-white to gray, vesicular to hollow, brittle stalactitic masses up to 20 cm (8 in.) in length.
Occurrence: The stalactitic material was most common at the Wanamie mine, as crusts on outcrops (Figure 41). Lesser amounts of stalactitic material were at Williamstown on the side of a steep depression. Both areas are very hot; at Wanamie the temperature ranges from 270 to >320°C (518 to >600°F). The white powder was found in lenticular deposits several centimeters below the surface of the culm at Williamstown at a relatively high temperature.
Associations: All $NH_4Al(SO_4)_2$ was intimately mixed with tschermigite. The compact powder also contained $Al_2(SO_4)_3$ or mascagnite.
Origin: The lenticular deposits could have formed by the evaporation of water carrying tschermigite in solution from the surface, or by direct sublimation. The origin of the stalactitic material may be similar; the flow of water carried dissolved tschermigite down the outcrop (at Wanamie) or into the depression (at Williamstown), where high temperatures quickly evaporated the water, resulting in the vesicular deposit.

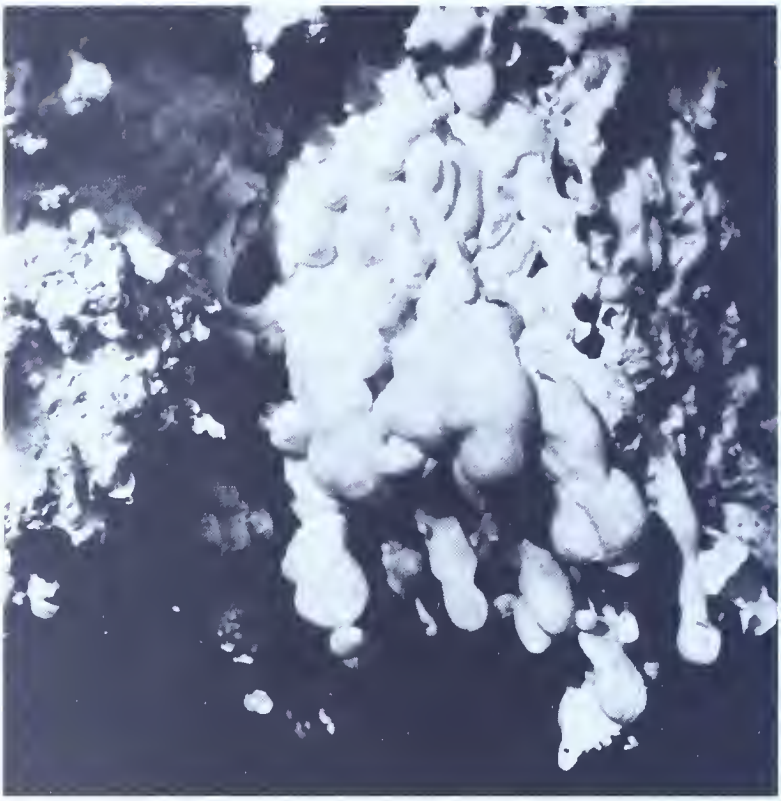

Figure 41. Stalactitic $NH_4Al(SO_4)_2$ at the Wanamie mine.

Identification: X-ray powder diffraction, semiquantitative emission-spectrographic analysis. Powder-diffraction data were compared to data for synthetic $NH_4Al(SO_4)_2$.

Aluminum Sulfate

Formula: $Al_2(SO_4)_3$

System: Hexagonal

Habit: White earthy masses of claylike powder.

Occurrence: Moderately abundant at the Williamstown waste pile, and in lesser amounts at Glen Lyon, as lenticular deposits up to 6 cm (2.4 in.) below the surface (Figure 42). Observed temperatures greater than 100°C (212°F); maximum below 300°C (572°F). Gradually hydrates at lower temperatures (approximately one third of sample hydrated to alunogen after storage at 20 to 25°C (68 to 77°F) for two years). Also a minor constituent of stalactitic masses at the Wanamie mine.

Associations: The lenticular deposits are intimate mixtures with alunogen, tschermigite, or $NH_4Al(SO_4)_2$. The stalactitic material is predominantly $NH_4Al(SO_4)_2$.

Figure 42. Massive $Al_2(SO_4)_3$ and alunogen from Williamstown.

Origin: Possibly from evaporation of water carrying sulfates in solution as it infiltrated the waste pile and encountered areas of temperatures greater than 100°C (212°F). $Al_2(SO_4)_3$ has been found associated with volcanic fumaroles (Stoiber and Rose, 1974).

Identification: X-ray powder diffraction, refractive index (1.468±.001), and chemical analysis (Al_2O_3, 21.53%; SO_3, 53.12; H_2O, 18.52; Fe_2O_3, 0.24; CaO, 0.01; $(NH_4)_2O$, <0.1; H_2O insoluble, 6.51; total <100.03%. The chemical analysis, combined with the diffraction data, indicates 54-56% $Al_2(SO_4)_3$ in a typical sample from Williamstown, the remainder being alunogen. A semiquantitative emission-spectrographic analysis was also performed. Powder-diffraction data were compared to data for synthetic $Al_2(SO_4)_3$.

Boussingaultite

Formula: $(NH_4)_2Mg(SO_4)_2 \cdot 6H_2O$
System: Monoclinic
Habit: Massive dark-red to yellow crust.

Occurrence: One sample, consisting of a linear streak 1 cm (0.4 in.) wide by 7 cm (2.8 in.) long on a charred piece of shale, was found during excavation of the Glen Lyon waste pile. The original position and conditions of formation were indeterminate.

Associations: Indeterminate. Sulfur present on specimen.

Origin: Probably by sublimation, possibly followed by hydration. Palache and others (1951, p. 455-456) listed fumaroles and a burning anthracite waste pile near Mahanoy City, Schuylkill County, as the only places where this mineral had been found.

Identification: X-ray powder diffraction.

Potassium Alum

Formula: $KAl(SO_4)_2 \cdot 12H_2O$

System: Cubic

Habit: Small (<100 μm, or <0.004 in.), clear, colorless crystals.

Occurrence: Found on one occasion at the Glen Lyon waste pile on a warm piece of wood near an active vent.

Associations: Sulfur.

Origin: Low-temperature alteration product. Palache and others (1951) noted that the mineral is derived by the action of sulfuric acid formed during the weathering of sulfides on alkali-rich aluminous silicates. Commonly occurs as an efflorescence in argillaceous rocks and coals containing sulfides. Associated minerals include alunogen, pickeringite, epsomite, gypsum, and sulfur.

Identification: X-ray diffraction, electron microprobe.

Tschermigite

Formula: $NH_4Al(SO_4)_2 \cdot 12H_2O$

System: Cubic

Habit: As small, colorless, fibrous or platy, isometric crystals, commonly in radial clusters, and, more commonly, as a white powder. Also as a minor constituent of vesicular stalactitic deposits (Figure 41).

Occurrence: The powdery variety was widespread on the surface, particularly in drainage channels (Figure 43), and was present in lenticular deposits 15 to 30 cm (6 to 12 in.) below the surface at the Glen Lyon and Williamstown waste piles. The crystals were also found on those waste piles. The stalactitic material was on an outcrop at the Wanamie mine and on the side of a depression at Williamstown.

Associations: Most samples, particularly the powder, contain some or all of the following: $NH_4Al(SO_4)_2$, mascagnite, The Geysers-type "mascagnite" (see section titled "Mascagnite"), alunogen, and $Al_2(SO_4)_3$. The stalactitic material is largely $NH_4Al(SO_4)_2$.

Figure 43. Tschermigite (white) lining drainage channels on the Williamstown waste pile.

Origin: Most probably forms by dissolution of $NH_4Al(SO_4)_2$ or other compounds by meteoric water, followed by evaporation at temperatures below 100°C (212°F). The stalactitic material could represent the hydration of $NH_4Al(SO_4)_2$ that formed by the same process above 100°C (212°F). Some tschermigite, particularly the crystals, could have formed by the reaction of ammonia-rich vapors with the shale.

Identification: X-ray powder diffraction, index of refraction ($n = 1.459 \pm .003$).

Gypsum

Formula: $CaSO_4 \cdot 2H_2O$

System: Monoclinic

Habit: Rounded clusters of intergrown waxy, yellowish crystals, each cluster approximately 1 mm (0.04 in.) in diameter; also as acicular radial aggregates of colorless transparent crystals approximately 5 mm (0.2 in.) in length. The latter crystals were light green when collected; the color faded after several weeks of storage at normal room temperature or within several minutes if heated.

Occurrence: The yellowish clusters were found in abundance over large areas of the surface of two small piles of shale on the Forestville waste pile, each about 8 to 10 m (26 to 33 ft) high by 10 to 20 m (33 to 66 ft) in diameter. The piles were warm, and had "steam" oozing from them. The larger, greenish crystals were collected around vents at the Wanamie mine.

Associations: Pickeringite at Forestville.

Origin: Gypsum has been reported previously as an efflorescence associated with fumaroles (Palache and others, 1951, p. 485). The occurrences described here indicate a relationship to gas evolution, perhaps by the reaction of evolved sulfurous gases with calcium in the substrate. Direct sublimation is possible but less likely.

Identification: X-ray powder diffraction, physical properties.

Hexahydrite and Epsomite

Formula: $MgSO_4 \cdot 6H_2O$ (hexahydrite); $MgSO_4 \cdot 7H_2O$ (epsomite)

System: Monoclinic (hexahydrite); orthorhombic (epsomite)

Habit: White, curvilinear, twisted prismatic aggregates 2 to 5 mm (0.08 to 0.2 in.) long by approximately ½ mm (0.02 in.) wide (Figure 44).

Occurrence: At the Wanamie mine at the bottom of a depression 1 m (3 ft) in diameter by 10 m (30 ft) deep. Temperature near 100 °C (212 °F).

Associations: Always found in intimate association with each other.

Figure 44. Hexahydrite and epsomite from the Wanamie mine.

Origin: Probably related to gas evolution, possibly by reaction of sulfurous gases with magnesium-bearing minerals. Uncertain whether epsomite formed simultaneously with hexahydrite at Wanamie or formed by hydration of hexahydrite after collection.

Identification: X-ray powder diffraction.

Pickeringite

Formula: $MgAl_2(SO_4)_4 \cdot 22\ H_2O$

System: Monoclinic

Habit: Tufts of white acicular needles about 1 mm (0.04 in.) long. Difficult to distinguish from alunogen without detailed analysis.

Occurrence: Found on one sample from Forestville.

Associations: Gypsum.

Origin: Low-temperature alteration product of sulfides. Palache and others (1951) noted that it is often observed as recent deposits in mine workings, especially in pyritic lignite or coal seams. It commonly forms as the weathering product of pyritic and aluminous material, accumulating as efflorescences in sheltered places.

Identification: X-ray powder diffraction and energy-dispersive X-ray spectroscopy.

Alunogen

Formula: $Al_2(SO_4)_3 \cdot nH_2O$, n = 16, 17, or 18.

System: Hexagonal

Habit: Most commonly as a component of an earthy white powder (Figure 42). One sample as trigonal, prismatic crystals that were green when collected, but became colorless within a few days at normal room conditions, similar to gypsum from the Wanamie mine.

Occurrence: The white powder is moderately abundant at the Glen Lyon and Williamstown waste piles and the Wanamie burning mine. It forms small surface deposits at all three locations and lenticular deposits as large as 1 m^2 (11 ft^2), 3 to 4 cm (1.2 to 1.6 in.) below the surface of the waste piles. The microscopic green crystals were found on a buried, rotting log approximately 4 to 6 cm (1.6 to 2.4 in.) below the surface of the Glen Lyon waste pile.

Associations: The white powder is a mixture. That from Williamstown contained $Al_2(SO_4)_3$, tschermigite, and minor alunogen. The other components of the powder from Glen Lyon and Wanamie could not be identified. No associated minerals were observed with the green crystals. The cause of the ephemeral green coloration could not be determined.

Origin: Has been previously reported associated with fumaroles and mine fires (Palache and others, 1951, p. 538-539). Probably similar origin to tschermigite.

Identification: X-ray powder diffraction. A chemical analysis and emission-spectrographic analysis were performed on the material from Williamstown (see section on $Al_2(SO_4)_3$).

SILICATE

Mullite

Formula: $Al_6Si_2O_{13}$
System: Orthorhombic
Habit: Straw-yellow prisms (approximately 100 μm, or 0.004 in.), more rarely as clear tabular crystals forming a matted layer on the surface of specular hematite (Figure 34).
Occurrence: Found in several "bomb" samples from Williamstown shortly after the passage of Tropical Storm Agnes in 1972. Apparently water seeping into the burning waste pile was vaporized. The rapidly expanding steam caused explosions that ejected material from the very hot interior of the pile, consisting of specular hematite and melted shale.
Association: Hematite.
Origin: Formed by high-temperature alteration of shales. The small size of the crystals indicates a minimum temperature of formation of 950 to 1000°C (1740 to 1830°F).
Identification: X-ray powder diffraction and energy-dispersive X-ray spectroscopy.

PARAGENESIS AND DISTRIBUTION

The paragenesis and distribution of the minerals forming on the burning coal-waste banks appear to be quite variable. Two methods of mineral formation were recognized, vapor deposition and alteration. Each of these may act alone or in concert to produce a given species. Distribution of the minerals is affected by the availability of chemical components, subsurface temperature, groundwater, surface water, humidity, and topography and drainage.

VAPOR DEPOSITION

Vapor deposition is probably the principal agent of mineral formation, either through direct sublimation from a vapor to a solid or, much more rarely, through the vapor-liquid-solid (VLS) growth mechanism.

Minerals that form by sublimation were observed throughout the upper 6 to 8 cm (2.4 to 3 in.) of the surface of the waste piles, the greatest concentrations occurring on the surface, in vent openings, and in cavities just below the surface. Their distribution is probably governed by temperature, mois-

ture, and the availability of components. Many of the sublimates are especially concentrated in sheltered areas, such as the underside of rocks near vents and in subsurface cavities. This might in part be a result of the harmful effects of weather on exposed delicate crystal forms and in part because of a higher concentration of evolved gases in sheltered areas. The high solubility of some of the minerals undoubtedly also contributes to this distribution pattern.

Sublimates also frequently exhibit a zonation around vents. This could be, in part, a function of the concentration of evolved gases. It can also be a function of temperature, as in the case of vents producing salammoniac (maximum condensation temperature = 340°C, or 644°F) near the opening and sulfur (melting point = 112.8°C, or 235.1°F) farther from the opening. The greater availability of atmospheric oxygen farther from the vent may also contribute to this zonation; for example, the presence of sulfates farther from a vent than native sulfur.

The presence or absence of certain compounds at various locations probably reflects differences in availability of components. For example, at Shenandoah, cryptohalite was found almost exclusively in areas that also had salammoniac. It thus appears either that a heterogeneous distribution of chlorine in the waste is here paralleled by a similar distribution of fluorine, or that conditions for the formation of these two minerals are similar and are met only in small, localized areas. Difference in availability of ammonia is an unlikely cause as mascagnite was abundant in areas at Shenandoah not occupied by salammoniac or cryptohalite. The absence of these ammonia compounds at other waste piles, despite the presence of other sulfates and halides, could reflect conditions unsuitable for the generation of ammonia. One mineral assemblage that is almost certainly dependent on local availability of an element is the assemblage of tin minerals found at Forestville (see section titled "Mineral Matter").

Temperature is important in controlling vapor deposition, as previously noted. Because many minerals sublime at temperatures near the upper limit of the range of stability, an increase in temperature could destroy existing phases and result in a new pattern of zonation. A lowering of temperature could result in a cessation of mineral production, or an inward migration of zones. Such a migration could result in superposition of crystals of one substance on those of another. A possible example of this was observed at a vent on the Glen Lyon waste pile which was surrounded by alternating layers of cryptohalite and selenium. Such variations in zonation could extend, as well, into the waste pile. Minerals would sublime from the vapors as appropriately lower temperatures were reached at increasing distances from the fire, and each zone would migrate as the fire changed. Where a zone intersected the surface of the bank, the minerals associated with the zone would crystallize around surface vents (see also Finkelman, 1978).

Vapor-liquid-solid growth has been described under GeS_2. This mechanism should be restricted by the same factors of temperature and availability as govern sublimation.

ALTERATION

A second agent of mineral formation is the alteration of sublimates and of primary rock components by heat, moisture, and evolved gases. Some effects brought about by heat have already been mentioned; e.g., the melting and resolidification of sulfur and the recrystallization of clay minerals in shale to form mullite. Experimentation suggests that the recrystallization of bararite to cryptohalite is also temperature-dependent, bararite forming at lower temperatures (Palache and others, 1951, p. 107).

One effect related to changes in temperature and humidity is the hydration and dehydration of sulfates. This is particularly notable for $NH_4Al_2(SO_4)_2$—tschermigite, and $Al_2(SO_4)_3$—alunogen. In both systems, the hydrous and anhydrous members were intermixed in every sample studied. As this is true of samples collected at temperatures above the stability range of the hydrous material, the anhydrous material apparently hydrates rapidly.

Another effect related to available moisture is the solution and recrystallization of some minerals. The massive, lens-like deposits of $NH_4Al(SO_4)_2$ and $Al(SO_4)_3$ found several centimeters below the surface of some waste piles may have formed as rainwater dissolved the ammonium and aluminum sulfates on the surface, carried them in solution while infiltrating the soil, then evaporated at the high temperatures encountered below the surface. A second example of solution and recrystallization is the very fine, chalky coating of tschermigite and other ammonium and/or aluminum sulfates found in drainage channels on the waste piles (Figure 43). Presumably, this material was carried in solution by rainwater runoff and thus was concentrated in the drainage channels.

Alteration of existing rock material and sublimates by the sulfurous gases is also suspected as, for example, suggested by Christie (1926) in the formation of cryptohalite and bararite (see bararite). Gypsum and some other sulfates could also be derived in this manner.

SOURCES OF COMPONENTS

GENERAL

Many of the minerals observed on the burning waste piles represent concentrations of rare and, in some instances, valuable elements. In view of

this, a brief survey of existing data on the mineralogy and trace-element geochemistry of the anthracite and associated sediments is warranted, with a view toward determination of the source of the elements.

Most of the elements released during combustion of the coal-waste-bank material probably are derived from the coal itself. Coal, however, is a complex mixture of organic and inorganic matter. The inorganic matter can be present as minerals, either detrital or authigenic, or as elements chemically bound to the organic matter.

Four main sources are postulated for the elements observed on the burning waste piles. These are (1) the organically bound minor and trace elements in the coal; (2) minerals introduced to the coal-bearing sequence before, during, or after coal deposition; (3) trace elements carried by groundwater; and (4) foreign material introduced into the waste piles by man.

PROVENANCE

The first three of the above-listed sources may have been strongly influenced by the provenance of the sedimentary rock of the region. Stratigraphic and sedimentologic studies of Pennsylvanian sediments in the Central Appalachian region (Meckel, 1967, 1970) indicate a general northwest to west direction of transport. Examination of lithologies to the east and southeast reveals a variety of available sources, such that a small difference in transport direction or distance might result in a significant difference in trace-element and mineral content of the anthracite basin.

Two possible source areas are the schists and gneisses of the Piedmont and the Precambrian to Lower Paleozoic formations of the Reading Prong.

CONCENTRATION BY PLANTS

The concentration of trace elements in coal depends in part on the life cycle of the coal-forming plants. Ten elements that are considered essential to all plant life, and that are normally enriched by plants, are C, O, H, N, P, K, Ca, Mg, S, and Fe (Miller, 1931). Additionally, certain plants selectively absorb certain other elements. Dead plants might also accumulate Si, Al, and rare elements including B, Cd, and Se (Ruch and others, 1974), whereas soluble compounds of Na, K, Ca, Mg, Fe, Mn, S, and P might be lost. These accumulation and depletion effects have been observed in the humus layers of modern forests (Abernathy and Gibson, 1963, p. 3).

Paleobotanical data concerning the Anthracite region are incomplete. Moreover, the biochemistry of the plants known to exist during the Pennsylvanian Period is open to speculation. Nevertheless, it is interesting to note the role of some inorganic elements in modern plants, as compiled from Gilbert (1949) and Day (1963), that might have been concentrated in

coal in significant quantities and that might have contributed to the sublimates:

Al: Probably not required for most plant species, although small amounts are found in the ash of all species. Certain plants, however, are Al accumulators. One example is the subdivision Lycopsida, which includes the important Pennsylvanian coal-forming trees *Lepidodendron* and *Sigillaria* and other associated plants (Darrah, 1969). Day (1963) reported 33 percent Al in ash of modern lycopsids. Other Al accumulators have been noted by Hutchinson (1945) and Hutchinson and Wollack (1943).

Si: Present in the ash of plants in greatly varying amounts. Amounts in excess of 50 percent have been reported in the ash of modern *Equisetineae* ("scouring rushes"). Grasses and similar plants contain large quantities of Si.

Ge: "It was shown by Goldschmidt that the germanium absorbed by plants tended to be concentrated in humus and ultimately in certain coals." (Day, 1963, p. 240).

N: Plants contain approximately 3 percent N in proteins. Most N is released from the organic matter by bacterial attack; however, some remains.

S: Required for plants; occurs chiefly in proteins and in volatile organic compounds.

Se: Poisonous to most plants in small quantities. However, certain plants are Se accumulators. The genus *Astragalus* includes species that utilize Se in the production of an amino acid, and is found only in areas where the soil has a high Se content (Shrift, 1969). Amounts ranging from 800 to 15,000 ppm Se in ash have been reported by Trelease (1945). Plants that require a relatively high quantity of S absorb an intermediate amount of Se; e.g., the family Cruciferae (Lakin, 1972).

F: Present in minute amounts in all plants, but has not been shown to be essential. A plant that might be an accumulator is the tea plant (400 ppm).

Cl: Present in plants, usually as NaCl. Na is required by plants, but Cl probably is not. There is no consensus on the mode of occurrence of Cl in coal. It appears to be in part organically bound and in part occurring in salts.

RANK OF COAL

Table 6 compares the concentrations of some elements in anthracite with concentrations in all ranks of coal. It is apparent that some particularly volatile elements, such as As and Cd, have lower concentrations in anthracite, probably due to the greater metamorphism undergone by these coals, whereas some less volatile elements, such as Al and Si, show modest increases, perhaps caused by relative concentration as the more volatile materials were removed. The concentrations of all elements in Table 6 are, of course, also influenced by many factors other than rank.

Table 6. *Average Amounts of 36 Elements in Coal and Shale*

Element	All coal [1] (799 samples)	Anthracite [1] (53 samples)	Average shale [2]
Si	2.6%	2.7%	7.3%
Al	1.4	2.0	8.0
Ca	.54	.07	2.21
Mg	.12	.06	1.55
Na	.06	.05	.96
K	.18	.24	2.66
Fe	1.6	.44	4.72
Mn	.01	.002	.085
Ti	.08	.15	.46
As	15 ppm	6 ppm	13 ppm
Cd	1.3	.3	.3
Cu	19	27	45
F	74	61	740
Hg	.18	.15	.4
Li	20	33	66
Pb	16	10	20
Sb	1.1	.9	1.5
Se	4.1	3.5	.6
Th	4.7	5.4	12
U	1.8	1.5	3.7
Zn	39	16	95
B	50	10	100
Ba	150	100	580
Be	2	1.5	3.0
Co	7	7	19
Cr	15	20	90
Ga	7	7	19
Mo	3	2	2.6
Nb	3	3	11
Ni	15	20	68
Sc	3	5	13
Sr	100	100	300
V	20	20	130
Y	10	10	26
Yb	1	1	2.6
Zr	30	50	160

[1] Swanson and others, 1976, Table 4C.
[2] Turekian and Wedepohl, 1961, Table 2.

GROUNDWATER GEOCHEMISTRY

The contribution by groundwater to the trace-element assemblage in the coal is uncertain, but probably significant. Two obvious effects are the removal of salts that are soluble at an acid pH, and the entrapment of metals as sulfides in the reducing environment of the coal. This could result in the

loss of Cl, F, Ca, K, and Na, and the gain of Pb, As, Se, and Fe, among others. Groundwater may also play a part in epigenetic mineralization, where sulfides, carbonates, and silicates are deposited in cleat and fractures in the coal.

FOREIGN MATTER

Foreign matter is present primarily in the waste piles, although it could also be present at the in-place coal seams, particularly where former mine workings have burned. Foreign matter includes anything that was not present in the strata prior to human intervention. There are no specific data on such material, but the list of possible contaminants is quite lengthy, particularly for the waste piles. Among them are mine timbers, iron and steel rails, lead pipes, waste from draft animals, truck tires, various animal-drawn and motorized vehicles, and general household trash. It is not uncommon for culm banks to be used as garbage dumps, although there was no apparent evidence of this practice at any of the banks studied.

Of the substances identified among the sublimates, those for which contribution from trash might be considered to have a relatively high possibility are Fe, Pb, Cu, Sn, and NH_3. S, Si, and Al have a somewhat lower likelihood of being, in part, trash derived. Those least likely to have had contributions from trash are Se, As, Cl, F, Mg, Ge, Bi, and K. These conclusions are, however, speculative, and the heterogeneity of the waste piles creates a situation such that a given element might be derived almost wholly from trash in a small area, but not at all elsewhere.

CHEMISTRY OF THE ANTHRACITE

Relatively few chemical analyses of Pennsylvania anthracite are available as compared to analytical data available on the bituminous coal of the western counties. Increasing attention has been focused on the anthracite reserves in recent years, however. Swanson and others (1976) included analyses of 36 elements for 53 Pennsylvania anthracite samples. These results are summarized in Table 6 and are compared with the average shale composition estimated by Turekian and Wedepohl (1961) and with average compositions determined for all ranks of coal. Of the elements listed, only Se is present in greater amounts in the anthracite than in the average shale. Because of the extreme heterogeneity of coal, however, average values may not be meaningful. The data in Table 6 are presented on a whole (unashed) coal basis from analyses either determined directly or calculated from data for ashed samples.

MODE OF OCCURRENCE OF THE ELEMENTS

Neither the chemical analysis of the coal nor a knowledge of the source of the elements is likely to reveal their mode of occurrence, that is, how the elements are currently bound in the coal. It is the mode of occurrence that will determine the behavior of an element in the burning coal-waste piles. The two broad categories of mode of occurrence are those elements that occur as minerals and those that are organically bound.

Organic Bonding

Relationships have been determined to calculate the probability of organic versus inorganic bonding of trace elements. Zubovic and others (1960) stated that small ions of high charge (i.e., ions that are not easily polarized) are preferred in organic bonding:

$$\frac{\text{ionic charge}}{(2)\,(\text{ionic radius})} \approx \text{likelihood of organic bonding} = \mu.$$

On the basis of this relationship, the following probabilities of organic versus inorganic bonding have been determined theoretically (elements in parentheses are additions to (+) or deletions from (−) these lists based on experimental work with Illinois coals by Ruch and others, 1974):

a) High probability of organic bonding ($\mu = 3.77 - 10.34$): Ge^{+4} (+B, +Be)
b) Moderate probability of organic bonding ($\mu = 2.54 - 3.38$): Bi^{+5}, Sn^{+4}
c) Low probability of organic bonding ($\mu = 0.15 - 2.42$): Bi^{+3}, Mg^{+2}, Zn^{+2}, Co^{+2}, Ge^{+2}, S^{-2}, Si^{-2} (+P, +Ti, +Sb, −Co)
d) High probability of inorganic bonding ($\mu = 0.38 - 0.83$): Pb^{+2}, Sn^{+2}, As^{+3}, Cu^{+1}, K^{+1} (+Co, +Ni, +Cr, +Se)

These calculations are consistent with the data of Zubovic (1966), who determined empirically that, in coal, Ge has high organic affinity, Co and Ni have intermediate affinities, and Zn, Sn, and Cu are largely inorganic. However, the apparent organic affinity of some elements, such as As^{+3} and Bi, may be due in part to a physical association of micrometer-sized accessory sulfides with the organic matter (Finkelman, Stanton, and others, 1979).

Volatility

As mentioned above, the volatility of an element may be a prime factor in the zonation of minerals around vents. The volatility of an element may also control its abundance on the surface of the burning waste pile. Sulfur and selenium, two of the most abundant elements in the sublimates, are

very volatile. Chalcophile elements that are also volatile were listed by Ahrens and Taylor (1961) as follows:

Element:	As ≈ Hg	> Sn ≈ Ge ≥ Cd >	Sb ≈ Pb ≥ Bi
Abundance:	6 0.15	<70 ~1.5 0.26	0.9 9.6 <1

This is roughly the order of abundance in which they are found in the sublimates. The values beneath the elements are their average concentration in ppm in anthracite from Pennsylvania. All but Bi are derived from Swanson and others (1976). The value for Bi is derived from unpublished studies of ash by Finkelman. Perhaps the reason Hg, Cd, and Sb minerals have not been observed as sublimates is because of their lower abundance in anthracite.

MINERALS IN COAL

The heat from the burning coal has the potential of liberating elements from minerals as well as from the organic matter in coal. This includes minerals in overlying and underlying units in the case of in-place burning seams, clastic rock fragments in the waste piles, and authigenic or detrital mineral matter incorporated in the coal. Eighty percent or more of the inorganic matter in coal was deposited as detritus or as precipitates from groundwater, or was introduced by metamorphism, hydrothermal activity, or secondary mineralization processes (O'Gorman, 1971).

A discussion of the mineralogy of individual rock-stratigraphic units in the region is of little value because the waste piles that produced most of the minerals under study include material derived from many different units. The sediments of this region consist principally of quartz and aluminosilicate minerals, and could be principal sources of Si, Al, and Fe.

Gluskoter (1975) noted that the overwhelming majority of minerals in coal are in one of four groups:

Aluminosilicates: illite, kaolinite, mixed-layer clays
Sulfides: pyrite, marcasite
Carbonates: calcite, siderite, ankerite, dolomite
Silica: quartz

Of these, the sulfide group could be one of the most important contributors to the sublimates. Elements observed in the minerals formed from burning anthracite that are common trace components in sulfides include Pb, As, Bi, Se, Fe, Ge, and Sn (Fleischer, 1955, p. 971). Various factors can, of course, influence the final mineral assemblage in coal. The authors have already mentioned the influence of the source area. Another factor is postdepositional alteration. Table 7 lists mineral assemblages observed by O'Gorman (1971) in the ash of five anthracite samples from two locations in Pennsylvania. Although these samples are restricted to the Southern Anthracite field, and are too small in number to allow generalizations to be

Table 7. *Major Mineral Content of Pennsylvania Anthracite Ash*

(in weight percent; after O'Gorman, 1971, p. 14 and 54)

Sample no.	Seam	Sample type	Location	Locality	Kaolinite	Illite	Quartz	Gypsum	Pyrite	Hematite	Rutile
81	Buck Mtn.	Lithotype	17.8–48.3 cm (7-19″) from top	Zerbe, Schuylkill County	>70	1–10	1–10	1–10	1–10	1–10	1–10
82	Buck Mtn.	Lithotype	78.7–99.1 cm (31-39″) from top	do.	>70	1–10	10–20	tr	1–10	n.d.	1–10
83	8½	Channel	—	Shamokin, Northumberland Co.	40–50	1–10	10–20	n.d.	1–10	1–10	1–10
84	8	Channel	—	do.	50–60	1–10	1–10	tr	1–10	n.d.	1–10
85	8 Leader	Channel	—	do.	50–60	10–20	1–10	1–10	1–10	1–10	1–10

tr = trace

n.d. = not determined

made, they suggest a possible major-mineral assemblage for Pennsylvania anthracite. Spackman and Moses (1960) found a similar assemblage of minerals in their study of coals from the Southern and Western Middle anthracite fields. Spackman and Moses detected the presence of calcite, pyrophyllite, and chlorite in several of their samples. Finkelman (1979) has detected the presence of sphalerite, chalcopyrite, galena, and linnaeite-group minerals in two Pennsylvania anthracites.

Samples 81 and 82 of O'Gorman (1971) in Table 7 are of particular significance to this study as Zerbe is only 5 km (3 mi) southwest of Forestville. Sample 82, from the Buck Mountain seam, is unusual in that it has 4,250 ppm Sn in low-temperature ash whereas most of O'Gorman's samples had <100 ppm Sn (O'Gorman, 1971, p. 92 and 105). More detailed, follow-up sampling of the Buck Mountain seam shows that the ash contains from 0.11 to 0.54 percent SnO_2, which X-ray diffraction revealed to be present as cassiterite (O'Gorman, 1971, p. 108 and 109). Additional studies by O'Gorman (1971) indicated that the Sn is present in inorganic mineral matter rather than in the organic fraction of the coal. Thus, the tin minerals observed on the burning waste pile at Forestville can probably be traced to the inorganic matter in the Buck Mountain seam.

Studies have recently been undertaken on identification of minerals in bituminous coal in western Pennsylvania (Finkelman, Dulong, and others, 1979; Cecil and others, 1979). These studies have indicated variable concentrations of kaolinite, illite, pyrite, quartz, calcite, dolomite, siderite, marcasite, rutile, anatase, gypsum, coquimbite, mixed-layer clays, montmorillonite, and plagioclase in low-temperature ash residues from the coal. Tentative identifications have been made of clausthalite and galena, which could serve as sources of Pb and Se.

SUMMARY OF SOURCES

Possible origins of the chemical components in the minerals found on the burning coal-waste piles can be inferred from the foregoing discussion:

Al: Common in enclosing sediments and in mineral matter in coal. Very high percentages possible in some coal-forming plants.

As: Sulfides are the most probable source (Minkin and others, 1979). Groundwater enrichment is possible.

Bi: Origin unknown.

Cl: Some organically bonded, some present as NaCl in coal and plants.

F: May be organically bonded; quantity in plants is variable. Could also be from minerals (e.g., apatite).

Fe: Probably contributed from all sources. It is a required nutrient in plants. Fe-bearing minerals are relatively common in coal and associated strata. Groundwater could contribute Fe from pyrite oxidation. Ferrous metals probably constitute a large part of the foreign matter in waste piles.

Ge: High probability of organic bonding. Ge can be absorbed and concentrated by plants.

K: Required for plants, but has a low probability of organic bonding. Could be derived from detrital minerals such as illite, mixed-layer clays, and muscovite.

NH_3: N and H are essential to all life and are very abundant in coal. Some contribution is also possible from organic trash.

Pb: Probably from sulfides and perhaps enriched by groundwater. Lead pipes and other trash are also possible sources.

S: Required by plants and very common in coal. Contribution from sulfides is most likely; possibly also some organic bonding. Possible contribution from organic trash in waste piles.

Se: Possible organic bonding; selectively absorbed and concentrated by certain plants, poisonous to others. Could also be contributed from inorganic minerals, especially sulfides (Minkin and others, 1979) and clausthalite.

Sn: Probably originated in detrital minerals, but also a likely constituent of trash (e.g., tin-plated cans, solder).

POTENTIAL UTILIZATION

Many of the materials present in the burning anthracite-waste piles have potential value. For example, sulfur, even though presently plentiful, has many uses in the chemical industry. Selenium and germanium are used in the electronics industry. Selenium is also used in glassmaking and in photocopy processes. Utilization of some trace metals could increase if they become more economically available.

A study by Sun and others (1971) concluded that it might be possible to extract alumina and silica from anthracite refuse. They further suggested (p. 54) " . . . a slight possibility of recovering germanium and/or gallium as a by-product of alumina extraction." Subsequent studies, reported by Charmbury and Chubb (1973), indicated that only alumina and silica might be extracted as marketable products. They also considered utilization of waste for building material, highway paving material, low-grade fuel, and as soilless media for the growth of plants. More recent studies by Cobb and others (1979) have demonstrated the feasibility of extracting coal and sphalerite from a waste pile in Illinois.

Little is known about the specific trace-element content of each waste pile. As technology changes, and as the economy fluctuates and the interest in using anthracite increases, the waste piles and the mined coal should be further examined as potential sources of As, Ge, Ga, Bi, Se, and Sn. Certain areas, such as the Forestville-Zerbe area, should be particularly pinpointed for further research in this regard as data compilations, such as that

of Swanson and others (1976), become available. Similar studies should be carried out in areas of lower rank, high-sulfur coal. It is possible that recovery of the more volatile trace elements could be achieved as part of a sulfur-removal system that will be required in the burning of medium- to high-sulfur coals.

ENVIRONMENTAL CONSIDERATIONS

The piles of waste that were left behind after decades of coal mining in this region and throughout Appalachia are, at best, ugly scars on the landscape. At their worst, burning waste piles produce clouds of noxious gases that can create a public health menace, as well as damage property. This problem is not new. It has existed for many decades. However, until recently, the problem was dismissed as the price of economic development. This attitude is reflected in the following quotation from a report published in 1928 (Sisler and others, p. 16–17):

> The large population and great wealth of the anthracite region is directly attributable to the occurrence and mining of anthracite. Before 1830 the valleys in the anthracite region were forested and were the sites of numerous small clearings where farmers were beginning to cultivate the fields. The discovery and subsequent development of anthracite has changed the appearance of the anthracite district. It is no longer a region of forest and fertile fields. Mine water has polluted most of the streams, the surface is scarred with holes where mine workings have fallen in, and enormous piles of rock, silt, and culm have accumulated. If anthracite were not being mined the valleys would be fertile farm lands, and the mountains between the valleys would be forested.
>
> In viewing the apparent destructiveness of mining one must not forget the great wealth which has come from this industry and the great benefit that it has been to the development of all of Pennsylvania's resources. The anthracite industry drew to Pennsylvania many of its Scotch, Welsh, and English pioneers. It has provided fuel for thousands of homes for 100 years; it has brought prosperity to thousands of people. The havoc which anthracite mining has done to the streams and forests in the anthracite field is nothing in comparison with the great influence it has had upon the development of Pennsylvania.
>
> The anthracite industry is the basic industry of the region. Without it the area would be depopulated. The pollution of streams by mine water, the silting of channels by waste material, and the destruction of vegetation by mining is a necessary evil of this industry.

The report continued by conceding that some improvements in the handling and disposal of waste material should be considered, particularly improvements that would neither curtail production nor increase the cost to the consumer. Potential uses of waste material were explored as one method of diminishing the problem.

Since that report was prepared, there has been a substantial decrease in mining activity in the anthracite district. Most of the mines and associated waste piles stand abandoned. In many instances, little, if any, effort was

made by the operator to correct the damage caused by his operation. The people who live in this region continue to pay the price of a bygone era of mining.

During the past decade, however, strides have been made in improving conditions in this region through "Operation Scarlift," administered by the Pennsylvania Department of Environmental Resources and the U. S. Bureau of Mines. At most of the waste piles described in this report the fires have been extinguished and major improvements have been made in reclaiming the land (Figures 45 through 53). However, many fires are still not extinguished, and many unburned waste piles and old mine workings pose less obvious hazards through the slow release of toxic substances via surface runoff and groundwater. Much remains to be learned about the interaction between the geochemical cycle and living organisms. Such interactions are known to be very complex. The sublimates observed indicate the presence of As, Se, and other potentially harmful substances. The harmful effects of many of these substances have been documented (Browning, 1961; Furst, 1971; Sax, 1957; Johnstone and Miller, 1961; Armstrong, 1971; Hadjimar-

Figure 45. A large smoking vent at Williamstown. Photograph was taken in 1974.

Figure 46. View from the top of the Williamstown waste pile in 1972 showing, at right, a reservoir constructed for extinguishment operations which were about to begin.

Figure 47. Looking toward the former site of the Williamstown burning waste pile, now reclaimed. Photograph was taken in 1979.

Figure 48. A part of the Forestville waste pile and, in the foreground, a reservoir constructed for extinguishment operations. Photograph was taken in 1974.

Figure 49. The same general area as shown in Figure 48, five years later, showing gradual establishment of vegetation after fire extinguishment. The slope on the left side of the picture was recently seeded.

Figure 50. The reservoir used in extinguishing the fire at the Kehley's Run mine at Shenandoah. Efforts to extinguish the fire were underway when this photo was taken in 1974.

Figure 51. Area of Kehley's Run mine in 1979, showing progress in land reclamation. Compare with similar view in Figure 8 (note building that has "Ice" sign in both photos).

Figure 52. The Glen Lyon waste pile while the fire was being extinguished in 1974. The broad, flat surface is the result of the excavating and grading of an area that had been burning. At the left is a water cannon used in quenching the fire.

Figure 53. Reclaimed Glen Lyon waste pile (grass covered, but treeless area near center of picture). Photograph was taken in 1979.

kos, 1973; Losee and Adkins, 1971; Louria and others, 1972; Shamberger and others, 1973).

Many of the elements present in coal are normally present in the soil of this and other areas. Some, such as Se, are possibly beneficial in the proper quantities. However, the large amounts of coal exposed in waste piles and abandoned strip mines worsen the situation by making available unusually large quantities of some elements of environmental concern. The burning seams and waste piles make the situation still worse by releasing the elements to the atmosphere or by creating readily soluble products. Concerted efforts should be made to remove the waste piles and the contaminants that they can release. Studies have found many potential uses for raw and incinerated anthracite refuse. Some has already been put to use for paving and construction (Figure 54).

With increasing shortages of energy sources, much consideration will be given to revitalizing the anthracite industry. Such a revitalization would produce a supply of relatively clean coal, and would provide economic help to a region of high unemployment. But the lessons of the past are clear. The mining of coal without proper efforts to restore the land potentially may

Figure 54. A small commercial operation for obtaining burned anthracite refuse, or "red dog," at Forestville.

take a toll in the health and property values of nearby communities and result in the waste of commodities that should ideally be recovered. The development of technology to use as much as possible of the material removed from a coal mine could produce a cleaner environment plus the dividend of new sources for essential commodities.

Meanwhile, further study of the contributions from waste piles to the trace- and minor-element composition of the air, soil, and water of the region would be beneficial. Such studies, carried out in conjunction with a compilation of health statistics for the region, would be of use in determining whether any harmful or beneficial effects are derived from the presence of this material.

CONCLUSIONS

The minerals that formed by vapor deposition in association with burning waste piles and anthracite seams include many never before described from Pennsylvania and several compounds previously undescribed as minerals. Most of the minerals probably formed by sublimation from a gas, and most of the others formed by subsequent alteration, primarily oxidation and hydration. At least one mineral is believed to have grown by the vapor-liquid-solid growth mechanism. The major factors that affect mineral formation are probably availability of components, temperature and temperature gradient, concentration of gases, protection from weather, and availability of oxygen and water.

All the fires substantially reduce the quality of life in nearby areas, both aesthetically and through the introduction of potentially harmful substances. The following suggestions are offered to reduce these problems in other locations:

(1) Efforts to extinguish the fires should continue.

(2) Extinguishment procedures should be conducted so that there is no chance of starting a coal-seam fire from burning waste; i.e., apparently extinguished waste should not be spread over areas of coal outcrop or in coal mines or shafts.

(3) After extinguishment, areas should be monitored by ground or infrared temperature measurements for at least two years, because fires that have been apparently extinguished have rekindled in the past.

(4) Precautions should be taken to prevent potentially hazardous substances from entering water supplies. Among such precautions that may be considered is the relocation of waste away from water supplies or places where drainage patterns lead directly to a stream, perhaps placing the waste on a montmorillonite base with a zeolite ion trap. Particularly dangerous has been the past practice of dumping waste in small stream valleys, where it not only polluted the water but created unstable dams.

(5) The lateral spread of underground fires might be stopped by excavation and the emplacement of noncombustible material to form a fire wall.

(6) Regulations requiring backfilling of strip mines, removal of waste piles, and regrading of the land should not be relaxed.

Recent studies have found potential uses for raw and incinerated anthracite refuse. It is hoped that economic utilization of this material will result from such studies, leading to the utilitarian removal of the refuse.

Until and unless practical uses are found, further study of the contribution of this material to the trace- and minor-element composition of the air, soil, and water of the region would be beneficial. Such studies carried out in conjunction with a compilation of health statistics for the region would be of use in determining whether any harmful or beneficial effects are derived from the presence of this material.

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